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Synthesis and Structural Characterization of Amidine, Amide, Urea and Isocyanate Derivatives of the Amino-*closo*-dodecaborate Anion $[B_{12}H_{11}NH_3]^-$

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Abstract: The synthesis and structural characterization of new derivatives of $[B_{12}H_{12}]^{2-}$ is of fundamental interest and is expected to allow for extended applications. Herein we report on the synthesis of a series of amidine, amide, urea and isocyanate derivatives based on the amino-*closo*-dodecaborate anion $[B_{12}H_{11}NH_3]^-$. Their structures have been confirmed by spectroscopic methods, and nine crystal structures are presented.

Keywords: dodecaborate; boron cluster; borane; amidine; amide; urea; isocyanate

1. Introduction

The *closo*-dodecaborate dianion $[B_{12}H_{12}]^{2-}$ (**1**, Figure 1) is an icosahedral boron cluster with 12 identical B–H vertices, and it possesses unique properties such as spherical electron delocalization and high thermal/chemical stability [1–4]. It is considered a 3D analogue of benzene, and applications of $[B_{12}H_{12}]^{2-}$ as well as its derivatives have been found in many fields, such as weakly coordinating anions [5–14], medicinal chemistry [15–17], catalysis [18,19], ligand design [20–22] and supramolecular chemistry [23–27].

Since the isolation of **1** in 1960 [28], many routes to substituted *closo*-dodecaborate anions have been reported *via* the construction of B–N, B–O, B–S, B–Hal or B–C bonds [29], and the ammonium dodecaborate $[B_{12}H_{11}NH_3]^-$ (**2**) serves as one of the fundamental building blocks for further functionalization [30]. Monoanionic **2** can be synthesized from the reaction of **1** with hydroxylamine-*O*-sulfonic acid (H_2N-SO_3H) on a multi-gram scale [30–32]. The $-NH_3$ site can be deprotonated under basic conditions and then combined with acyl chlorides, carbodiimides or aldehydes to afford the corresponding amides **3** [33–37], guanidines **4** [34] and imines **5** [38]. Dodecaborate amidines **6** have not been explored yet, and urea derivatives **7** were unknown until we recently found that the reaction of **2** with dialkylcarbamoyl chlorides $ClC(O)NMe_2$ or $ClC(O)NEt_2$ affords the corresponding $\{B_{12}\}$-substituted *N*,*N*-dialkyl ureas [39]. The isocyanate derivative **8** was originally synthesized from the reaction of the carbonyl derivative $[B_{12}H_{11}(CO)]^-$ with NaN_3 but characterized only by ^{11}B-NMR and IR spectroscopy [40]. Herein we present: (1) the synthesis of three new $\{B_{12}\}$-based amidines **6** with two crystal structures; (2) six crystal structures of $\{B_{12}\}$-based

amides **3** and a simple approach for the interconversion between their dianionic and monoanionic forms; (3) the synthesis of two new $\{B_{12}\}$-based aromatic ureas **7**; (4) a new route to isocyanate **8** and its crystal structure.

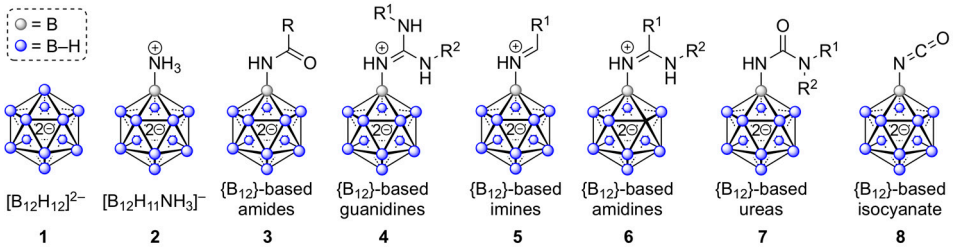
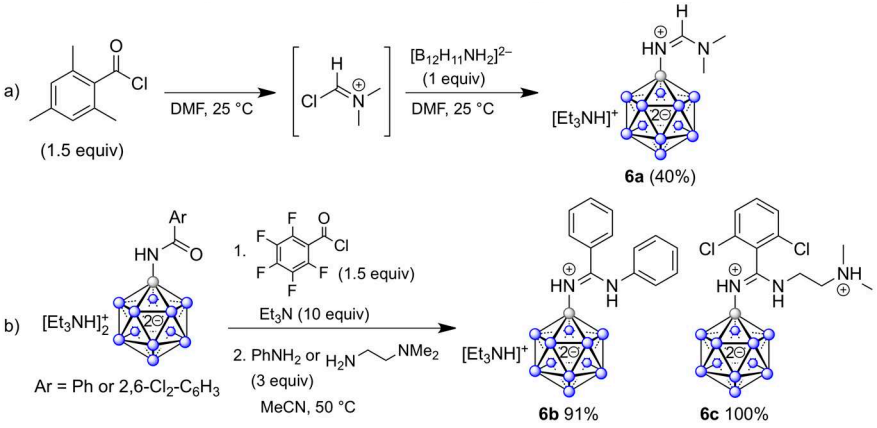


Figure 1. General structures of the parent *closo*-dodecaborate dianion $[B_{12}H_{12}]^{2-}$ and its derivatives.

2. Results and Discussion

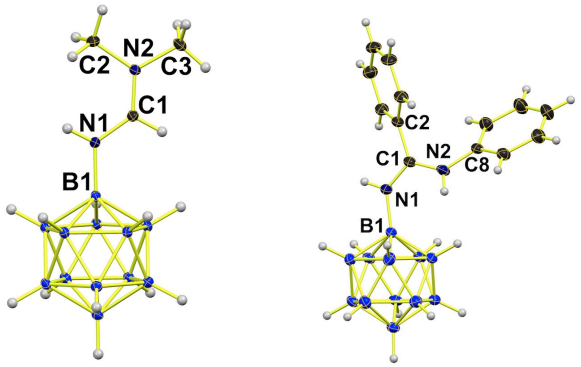
2.1. Synthesis of {B12}-based Amidinium Ions

Amidine derivatives based on the $\{B_{12}\}$ cluster have not been reported before, and in the following, methods to synthesize them are presented. Combination of dimethyl formamide with 2,4,6-trimethylbenzoyl chloride afforded the chloroiminium intermediate, which upon attack by $[B_{12}H_{11}NH_2]^{2-}$ afforded **6a** (Scheme 1a). This reaction allowed for the isolation of the desired product; however, the yield of 40% was moderate, and furthermore extension of the substrate scope by this method did not appear convenient. Using a related strategy, we found that the carbonyl group of $\{B_{12}\}$-based amides can be activated by pentafluorobenzoyl chloride, and subsequent attack by amines would then lead to $\{B_{12}\}$-based amidinium ions (Scheme 1b). Following this approach, products **6b** and **6c** were isolated in excellent yields of 91% and 100%, respectively.



Scheme 1. Synthesis of $\{B_{12}\}$-based amidinium ions **6a–c** using (**a**) the chloroiminium intermediate derived from dimethylformamide and (**b**) pentafluorophenylbenzoyl chloride as activating agent.

Single crystals of **6a** and **6c** were obtained from acetonitrile solutions, and ORTEP representations of **6a** and **6c** are displayed in Figure 2. Observed distances (Å) are B1–N1 1.520(2), N1–C1 1.3078(18), C1–N2 1.3092(19), N2–C2 1.451(2) and N2–C3 1.4662(19) for **6a**; B1–N1 1.534(4), N1–C1 1.312(4), C1–N2 1.331(4), C1–C2 1.485(4) and N2–C8 1.420(4) for **6b**. These structural features are similar to those of typical organic amidinium ions; in addition, the coordination geometry around C1 is perfectly trigonal-planar for both products with a sum of angles of 360°. The torsion angles N1-C1-N2-C2 and N1-C1-N2-C3 of **6a** are 0.0(2) and –175.35(15)°, respectively, indicating coplanarity of the amidine and the dimethylamino moieties. On the other hand, **6b** is more twisted with a torsion angle N1-C1-N2-C8 of 154.4(3)°.

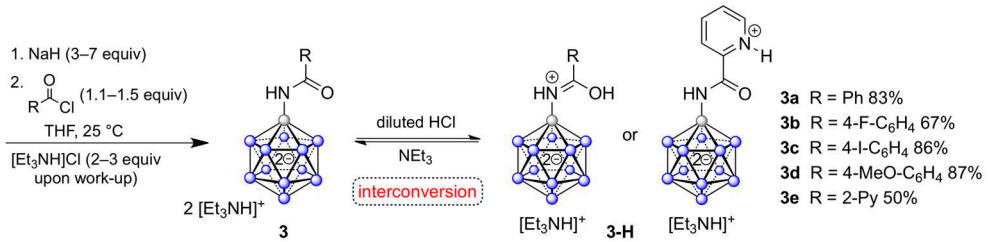


(**a**) (**b**)

Figure 2. Crystal structures of (**a**) **6a** and (**b**) **6b**; cations and solvent molecules are omitted for clarity, and thermal ellipsoids are displayed at the 30% level.

2.2. Synthesis of {B_{12}}-based Amides

{B_{12}}-based amides **3** were originally synthesized by other groups [33–36]. The products were isolated in their *O*-protonated form **3-H**, and there was only one crystal structure reported, namely **3a-H** with R = Ph (Scheme 2). Our group recently modified the reaction conditions, and the products were obtained in up to 95% yields in the *O*-deprotonated form **3** after chromatography on silica gel [36]. Our approach uses smaller amounts of acyl chlorides and a slight excess of sodium hydride base, which results in the isolation of the dianionic form (for this study, **3a–d** were resynthesized according to [37] in order to probe their solid-state structures). Adjustment of the pH value with diluted hydrochloric acid during the work-up or after isolation leads to **3-H** in their *O*-protonated form. Back-conversion to **3** can be achieved by dissolution in MeCN, treatment with Et_3N and distillation of all the volatiles. Pyridine-substituted **3e** was synthesized as a new product. Since purification by chromatography proved difficult, it was isolated as **3e-H** in 50% yield upon acidic work-up and recrystallization from methanol. Conversion to **3e** occurred quantitatively using the above-mentioned procedure. In contrast to previously described amides, protonation of **3e** takes place at the pyridine ring, indicating the higher basicity of the heterocycle as compared to the amide moiety. The $^{11}B\{^1H\}$-NMR spectra of **3b**, **3b-H**, **3e** and **3e-H** are shown in Figure S1 as representative examples to demonstrate the effect of protonation. For R = Ph (**3a**), 4-F-C_6H_4 (**3b**), 4-I-C_6H_4 (**3c**) 4-MeO-C_6H_4 (**3d-H**), 2-pyridyl (**3e**) and 2-pyridyl-H (**3e-H**), crystal structures were elucidated, and selected structural features are discussed below.



Scheme 2. Synthesis of {B_{12}}-based amides **3** and interconversion between their dianionic and monoanionic forms; compounds **3a–d** were prepared according to [37].

Single crystals of **3a**, **3b**, **3c**, **3d-h**, **3e** and **3e-H** were obtained from acetonitrile, acetone, acetonitrile-acetone or acetonitrile-methanol solutions. ORTEP representations are displayed in Figure 3, and a summary of structural parameters is given in Table 1, including data for *O*-protonated **3a-H**, originally reported by Gabel and coworkers [34]. The seven compounds can be grouped into the series **3a**/**3b**/**3c**/**3e**/**3e-H** and **3a-H**/**3d-H**. For the former series, distances (Å) fall within B1–N1 1.51–1.52, N1–C1 1.31–1.33 and C1–O1 1.23–1.25. These compounds thus exhibit strong structural resemblence to classical organic amides. For the latter pair, observed ranges (Å) are B1–N1 1.53–1.58,

N1–C1 1.26–1.30 and C1–O1 1.31–1.34. These values are consistent with O-protonation, leading to a more pronounced allyl cation-type equalization of bond lengths. On the other hand, all seven products share two features: The central carbon atom C1 has perfect trigonal-planar geometry with a sum of angles of 360°. Furthermore, the torsion angles O1-C1-C2-C3 (O1-C1-C2-N2 for **3e-H**) fall in the range of –18° to +32° and indicate a certain degree of conjugation between the aromatic rings and the N1-C1-O1 π system.

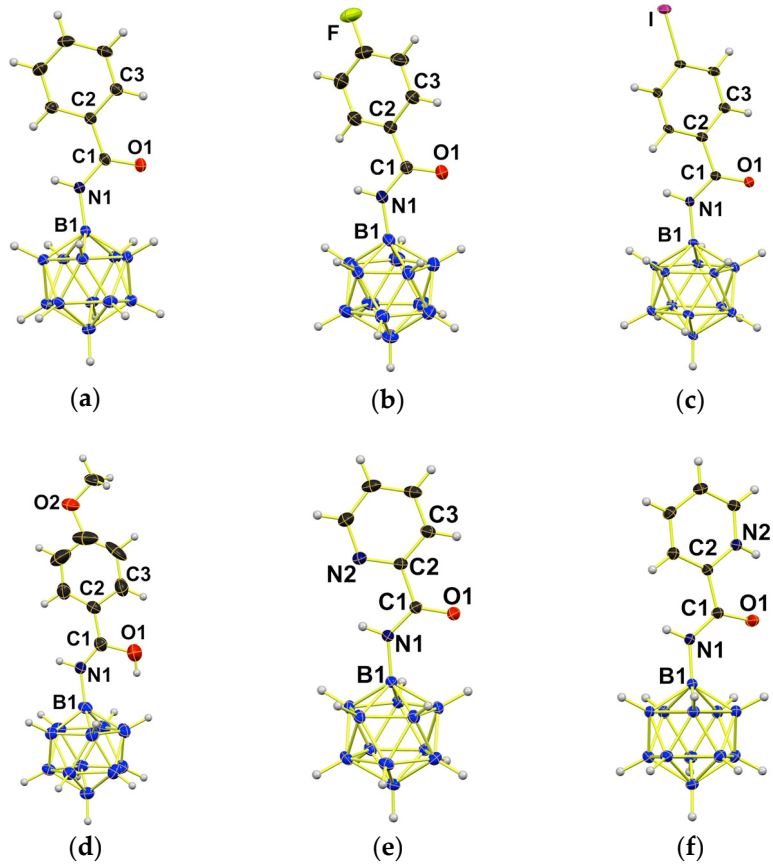


Figure 3. Crystal structures of (**a**) **3a**, (**b**) **3b**, (**c**) **3c**, (**d**) **3d-H**, (**e**) **3e** and (**f**) **3e-H**; cations and solvent molecules are omitted for clarity, and thermal ellipsoids are displayed at the 30% level.

Table 1. Selected bond lengths and angles for **3a**, **3a-H** **3b**, **3c**, **3d-H**, **3e** and **3e-H**.

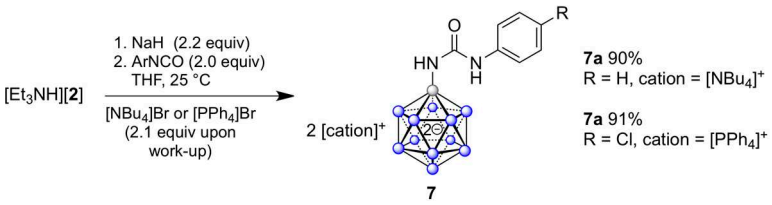
Distance [Å]/Angle [°]	3a [1]	3a-H [2]	3b	3c	3d-H	3e	3e-H
B1–N1	1.520(6)	1.534(4)	1.516(4)	1.512(5)	1.577(7)	1.516(3)	1.524(3)
N1–C1	1.324(6)	1.295(7)	1.320(4)	1.327(4)	1.263(7)	1.306(2)	1.316(3)
C1–O1	1.250(5)	1.314(2)	1.238(3)	1.227(4)	1.343(8)	1.234(2)	1.232(3)
C1–C2	1.496(6)	1.471(2)	1.500(4)	1.500(5)	1.466(17)	1.502(3)	1.512(3)
Σ(C1)	359.9	359.9	360.0	360.0	359.9	360.0	360.0
O1-C1-C2-C3 [3]	–17.8(3)	–9.95(13)	–15.6(4)	32.0(3)	–4.9(4)	5.77(2)	7.4(3)

[1] Parameters of one of the two molecules in the asymmetric unit; [2] data from reference [34]; [3] torsion angle O1-C1-C2-N2 for **3e-H**.

2.3. Synthesis of {B_{12}}-based Ureas

{B_{12}}-based ureas with *N*{B_{12}},*N*′(aryl) substitution have not been reported before. The synthetic strategy to prepare dodecaboranyl *N*,*N*-dialkyl ureas recently reported by our group involved the combination of **2** with dialkylcarbamoyl chlorides [39]. We wondered whether aromatic isocyanates could be used instead of carbamoyl chlorides to achieve the new substitution pattern, given the

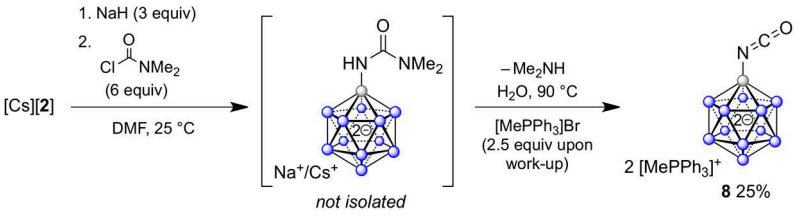
commercial availability of many ArNCO reagents. We found that the reaction of **2** with aromatic isocyanates under basic conditions directly leads to the formation of the corresponding urea derivatives of the structure $\{B_{12}\}$NH-C(O)-NHAr. Thus, the transformations with commercially available PhNCO and 4-Cl-C_6H_4NCO cleanly gave products **7a** and **7b** in yields of 90% and 91% (Scheme 3). They were isolated by precipitation upon cation exchange to $[NBu_4]^+$ or $[PPh_4]^+$ and characterized by NMR spectroscopy and mass spectrometry.



Scheme 3. Synthesis of $\{B_{12}\}$-based ureas **7**.

2.4. Synthesis of Dodecaboranyl Isocyanate

Isocyanates are important intermediates in organic synthesis that are used in the manufacture of, e.g., agrochemicals and polyurethanes [41]. Only one publication by Alam and coworkers from 1989 mentioned the isolation of dodecaboranyl isocyanate **8** [40]. It was prepared *via* the reaction of $[B_{12}H_{11}(CO)]^-$ with NaN_3 and analyzed by ^{11}B-NMR and IR spectroscopy. However, further characterization was not given, and in particular the crystal structure was not reported. Because the isocyanate moiety serves as versatile functional group handle capable of providing access to a number of novel $\{B_{12}\}$-based derivatives, we were interested in resynthesizing **8**. However, multiple attempts to reproduce the original procedure were not successful in our laboratory, and we therefore sought to establish an alternative route. Since dodecaboranyl *N*,*N*-dialkyl ureas can be prepared easily [39], their thermal fragmentation appeared as an attractive strategy. Indeed, treatment of **2** with base and $ClC(O)NMe_2$ to give the intermediate urea, followed by heating in water, afforded **8** in 25% overall yield (Scheme 4). The yield of this sequence is rather low, and efforts to improve the protocol are ongoing.



Scheme 4. Synthesis of isocyanate **8**.

In acetonitrile-d_3 solution, the ^{11}B NMR shifts of **8** were −7.7, −15.4, −16.7 and −19.3 ppm, while ^{1}H NMR resonances appeared at 1.23, 0.97 and 0.75 ppm. The NCO ^{13}C NMR signal could not be detected unambiguously; it is known from organic isocyanates that this signal can be very broad and difficult to observe. Interestingly, **8** is inert towards air and moisture. Solutions in acetone, kept under ambient conditions, remained unchanged over six months. The IR spectrum showed characteristic absorbtions at 2479 cm^{-1}, 2308 cm^{-1} and 1438 cm^{-1} stemming from B–H, $\nu_{asymmetric}$(NCO) and $\nu_{symmetric}$(NCO) stretchings, respectively (Figure 4a) [42].

Colorless single crystals of **8** were obtained from acetone solution. X-Ray diffraction revealed distances (Å) of B1–N1 1.499(3), N1–C1 1.138(3) and C1-O1 1.186(3), clearly indicating the two double bonds of the N=C=O moiety (Figure 4b). This finding is in agreement with the angle N1-C1-O1 of 176.5(3)°, showing almost linear geometry of the isocyanate group. The B1-N1-C1 angle of 163.1(3)° is also quite large, while no unusual structural features were observed for the $\{B_{12}\}$ cluster.

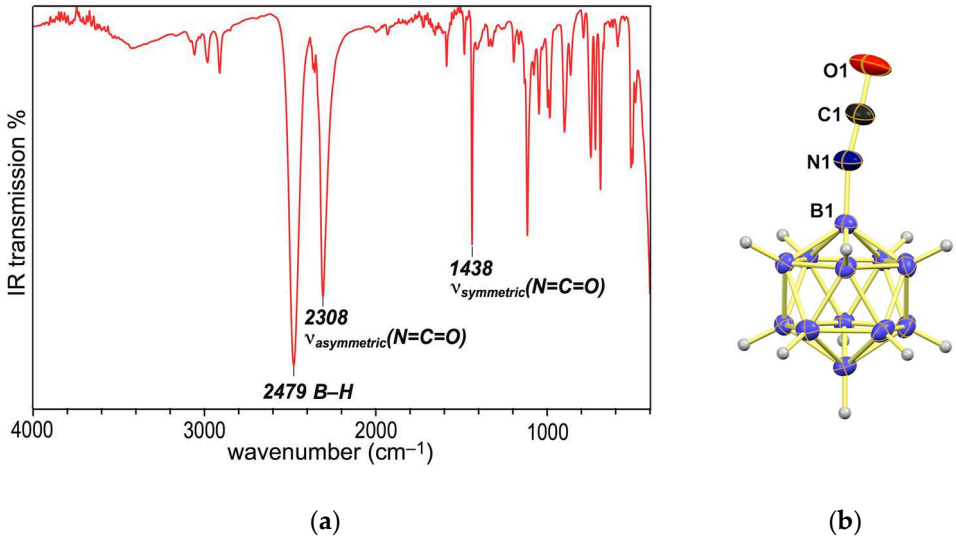


Figure 4. (**a**) IR spectrum and (**b**) crystal structure of $[MePPh_3]_2[B_{12}H_{11}NCO]$; cations in the crystal structure omitted for clarity, thermal ellipsoids displayed at the 30 % level.

3. Materials and Methods

3.1. General

If not otherwise specified, reagents and organic solvents were commercially available and used without further purification. Anhydrous solvents were prepared by passage through activated Al_2O_3 and stored over 3 Å molecular sieves. CD_3CN and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories and filtered through Al_2O_3 prior to use. $[B_{12}H_{12}]^{2-}$ and $[B_{12}H_{11}NH_3]^-$ salts and dodecaborate amides **3a**–**e** were prepared according to the literature [10,36].

Glassware for air-sensitive reations was dried at 150 °C and allowed to cool in a vacuum. Reactions carried out in a glovebox were run under a nitrogen atmosphere with O_2, H_2O < 1 ppm.

Thin-layer chromatography (TLC) was carried out using silica gel 60, F254 with a thickness of 0.25 mm. Column chromatography was performed on silica gel 60 (200–300 mesh).

Low-resolution ESI-MS data were recorded on Advion Expression CMS instrument (Advion, Ithaca, NY, USA). High-resolution MS data were recorded using IT-TOF detection (Shimadzu, Kyoto, Japan) equipped with an electrospray ionization source (ESI). Accurate mass determination was corrected by calibration using sodium trifluoroacetate clusters as a reference.

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Gemini A Ultra diffractometer (Agilent Technologies, Santa Clara, CA, USA) equipped with an 135 mm Atlas CCD detector and using Mo K-a radiation.

NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (^{1}H NMR 500.13 MHz, ^{13}C NMR 125.77 MHz, ^{11}B NMR 160.46 MHz) or a Bruker AVANCE III 400 spectrometer (Bruker, Billerica, MA, USA) (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, ^{11}B NMR 128.38 MHz) at the temperature indicated. Data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. Signals were referenced against solvent peaks (^{1}H: residual $CHD_2C(O)CD_3$ = 2.05 ppm, residual CHD_2CN = 1.94 ppm, residual $CHDCl_2$ = 5.32 ppm, $^{13}C\{^1H\}$: $CD_3C(O)CD_3$ = 29.84 ppm, CD_3CN = 1.32 ppm, CD_2Cl_2 = 53.32 ppm). ^{11}B and $^{11}B\{^1H\}$ NMR spectra were calibrated against external BF_3*Et_2O = 0 ppm (BF_3*Et_2O capillary in C_6D_6).

3.2. Experimental Section

Synthesis of [Et_3NH](**3e-H**): In a glovebox filled with N_2, a 20 mL vial was charged with $[Et_3NH][B_{12}H_{11}NH_3]$ (212.4 mg, 0.817 mmol, 1 equiv), NaH (138.2 mg, 5.758 mmol, 7 equiv) and a stir

bar. THF (4 mL) and DMF (4 mL) were added, and the mixture was stirred at room temperature for 10 min until there was no H_2 evolution anymore. Then pyridine-2-carbonyl chloride hydrochloride PyCOCl·HCl (220.2 mg, 1.237 mmol, 1.5 equiv) was slowly added. The conversion was complete after stirring for 5 h. The flask was transferred out of the glovebox. H_2O (4 mL) was added, and the pH value of the reaction mixture was adjusted to 2–3 with 1 M aqueous HCl. [NEt_3H]Cl (300 mg, 2.180 mmol, 2.7 equiv) was added, and the reaction mixture was extracted with MeCN/EtOAc (1:2 *v*/*v*). The organic layers were concentrated on a rotary evaporator. The residue was purified by recrystallization from methanol to afford yellowish crystals of [Et_3NH][**3e-H**] (150 mg, 50%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.96 (s, 1H, anionic NH), 8.90–8.86 (m, 1H, Py H), 8.18–8.14 (overlapping m, 2H, Py H), 7.89–7.72 (m, 1H, Py H), 6.63 (t, 1H, J_{NH} = 52 Hz, NH), 3.27 (s, 1H, NH), 3.20–3.15 (m, 6H, cationic N–CH_2), 1.47 (broad signal, 5H, B–H), 1.24 (t, *J* = 7.4 Hz, 9H, cationic CH_3), 1.20 (broad signal, 5H, B–H), 1.13 (broad signal, 1H, B–H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 166.7, 149.5, 143.9, 141.5, 129.8, 124.5 (6 anionic signals), 48.0, 9.2 (2 cationic signals). $^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = –7.6 (1B, B–N), –15.3 (5B, B–H), –15.7 (overlapping signals, 6B, B–H). High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_6H_{17}B_{12}N_2O]^-$ 263.2430. Found: 263.2459.

Transformation of [Et$_3$NH](**3e-H**) *to [Et$_3$NH]$_2$*(**3e**): A 20 mL vial was charged with [Et_3NH][**3e-H**] (50 mg) and a stir bar. MeCN (3 mL) and Et_3N (0.5 mL) were added, and the solution was stirred at room temperature for 1 h. Then the stir bar was removed, and the solution was concentrated on a rotary evaporator and dried overnight under vacuum at 80 °C to afford compound [Et_3NH]$_2$[**3e**] in quantitative yield. This method can also be applied for the transformation of other compounds **3-H** to **3** quantitatively. $^{11}B\{^1H\}$ NMR spectra of **3b**, **3b-H**, **3e** and **3e-H** are displayed in Figure S1. $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.56 (broad signal, 1H, Py H), 8.09–8.00 (m, 1H, Py H), 7.99–7.80 (overlapping m, 2H, Py H and amide N–H), 7.50–7.38 (m, 1H, Py H), 4.63 (broad t, 2H, J_{NH} = 52 Hz, N–H from cation), 3.25–3.01 (m, 12H, cationic N–CH_2), 1.34 (s, 5H, B–H), 1.24 (t, *J* = 7.4 Hz, 9H, cationic CH_3), 1.03 (broad signal, 5H, B–H), 0.89 (broad signal, 1H, B–H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 166.2, 152.9, 149.0, 138.5, 126.4, 122.2 (6 anionic signals), 47.8, 9.1 (2 cationic signals). $^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = –5.3 (1B, B–N), –15.3 (5B, B–H), –16.4 (5B, B–H), -18.7 (1B, B–H). High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_6H_{17}B_{12}N_2O]^{2-}$ 131.1226. Found: 131.1254.

Synthesis of amidine [Et$_3$NH](**6a**): In a glovebox, a dry 20 mL vial, equipped with a stir bar, was charged with [Et_3NH][$B_{12}H_{11}NH_3$] (102 mg, 0.40 mmol, 1 equiv). Then anhydrous DMF (1 mL) was added. The vial was transferred to a fumehood, and dry Et_3N (1.0 mL, 7.20 mmol, 18 equiv) was added to the solution under N_2 protection. Then 2,4,6-trimethylphenylcarboxylic acid chloride (110 mg, 0.60 mmol, 1.5 equiv) was added. The mixture was stirred at 25 °C for 4 h. The reaction was quenched with an aqueous [Et_3NH]Cl solution (2 mL H_2O + 2 equiv [Et_3NH]Cl); the pH value at this point was ca. 7–8. The mixture was extracted with DCM/MeCN = 4: 1 (8 × 10 mL). The combined organic layers were dried over $MgSO_4$, and the solution was filtered and concentrated by rotary evaporation. The cloudy residue was purified by silica gel column chromatography (eluent DCM/MeCN = 10:3, fraction size 20 mL). The combined eluates were concentrated on a rotary evaporator and dried under vacuum at 60 °C overnight to afford compound [Et_3NH][**6a**] as a colorless solid (50.4 mg, 40%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN, 23 °C): δ 7.76 (d, *J* = 16.0 Hz, 1H, N=CH–N), 6.41 (broad signal, 1H, N–H), 3.13 (q, *J* = 7.2 Hz, 6H, cationic N–CH_2), 3.08 (s, 3H, anionic N–CH_3), 2.83 (s, 3H, anionic N–CH_3), 1.26 (broad signal, 5H, B–H), 1.24 (t, *J* = 7.2 Hz, 9H, cationic N–CH_2CH_3), 1.03 (broad signal, 5H, B–H), 0.85 (broad signal, 1H, B–H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 23 °C): δ 157.3 (N=C–N), 48.0 (cationic CH_2), 43.1, 35.7 (two N–C signals), 9.2 (cationic CH_3). $^{11}B\{^1H\}$ NMR (160 MHz, CD_3CN, 23 °C): δ −4.2 (1B, B–N), −14.5 to −17.0 (10B, B–H), −19.0 (1B, B–H). High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_3H_{19}B_{12}N_2]^-$: 213.2738. Found: 213.2762.

Synthesis of amidine [Et$_3$NH](**6b**): A dry 20 mL vial, equipped with a stir bar, was charged with [Et_3NH]$_2$[$B_{12}H_{11}NHCOC_6H_5$] (101 mg, 0.22 mmol, 1 equiv). Then anhydrous MeCN (3 mL) was added, and dry Et_3N (0.3 mL, 2.16 mmol, 9.8 equiv) was added to the solution under N_2 protection.

Pentafluorophenylcarboxylic acid chloride (80.0 mg, 0.35 mmol, 1.5 equiv) was added at 25 °C. The temperature was raised to 50 °C. After 30 min, aniline (61 mg, 0.66 mmol, 3.0 equiv) was added. The mixture was stirred for another 4 h and concentrated by rotary evaporation. The cloudy residue was purified by silica gel column chromatography (eluent DCM/MeCN = 4:1, fraction size 20 mL). The combined eluates were concentrated on a rotary evaporator and dried under vacuum at 60 °C overnight to afford compound $[Et_3NH]$[**6b**] as a yellow solid (87.7 mg, 91%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2, 23 °C): δ 10.00 (s, 1H, N–H), 7.53–7.48 (m, 1H, phenyl H), 7.41–7.35 (overlapping m, 4H, phenyl H), 7.24-7.09 (overlapping m, 3H, phenyl H), 7.03–6.78 (overlapping broad signal and m, 3H, phenyl H and N–H), 6.65 (broad signal, 1H, N–H) 3.29–3.22 (m, 6H, cationic N–CH_2), 1.62 (broad signal, 5H, B–H), 1.40 (t, J = 7.2 Hz, 9H, cationic N–CH_2CH_3), 1.22 (broad signal, 5H, B–H), 1.05 (broad signal, 1H, B–H). This spectrum contained small signals at 7.18, 6.71 and 6.67 ppm ascribed to residual aniline. $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 23 °C): δ 165.6 (N=C–N), 138.1, 133.2, 131.3, 130.4, 130.1, 129.9, 127.5, 125.6 (8 aryl signals), 48.3 (cationic N–CH_2), 9.4 (cationic N–CH_3). This spectrum showed small signals at 149.1, 130.2, 118.3 and 115.6 ppm ascribed to residual aniline. $^{11}B\{^1H\}$ NMR (128 MHz, CD_2Cl_2, 23 °C): δ −5.8 (1B, B–N), −13.5 to −16.5 (10B, B–H), −17.4 (1B, B–H). High-resolution ESI-MS (negative mode, MeOH): m/z calcd for $[C_{13}H_{23}B_{12}N_2]^-$: 337.3056. Found: 337.2382.

Synthesis of amidine [Et_3NH](**6c**): A dry 20 mL vial, equipped with a stir bar, was charged with $[Et_3NH]_2[B_{12}H_{11}NHCOC_6H_3Cl_2]$ (177 mg, 0.33 mmol, 1 equiv). Then anhydrous MeCN (3 mL) was added, and dry Et_3N (0.45 mL, 3.25 mmol, 9.8 equiv) was added to the solution under N_2 protection. Pentafluorophenylcarboxylic acid chloride (128 mg, 0.55 mmol, 1.7 equiv) was added at 25 °C. The temperature was raised to 50 °C. After 30 min, *N*,*N*-dimethylethylamine (88 mg, 1.00 mmol, 3.0 equiv) was added. The mixture was stirred for another 4 h, and 1 M aqueous HCl (5 mL) was added. The suspension was extracted with EtOAc/MeCN 3:1 (5 × 10 mL). The combined organic layers were dried over $MgSO_4$, and the solution was filtered and concentrated by rotary evaporation. The cloudy residue was purified by silica gel column chromatography (eluent DCM/MeCN = 4:3, fraction size 20 mL). The combined eluates were concentrated and dried under vacuum at 60 °C overnight to afford compound $[Et_3NH]$[**6c**] as a yellow solid (132 mg, 100%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN, 23 °C): δ 8.54 (broad signal, 1H, N–H), 7.59–7.55 (overlapping m, 3H, aryl H), 7.46 (broad signal, 1H, N–H), 6.98 (very broad signal, 1H, N–H), 3.43 (dt, J = 7.2 Hz, 7.2 Hz, 2H, CH_2), 3.24 (t, J = 7.2 Hz, 2H, CH_2), 2.77 (s, 6H, N–CH_3), 1.41 (broad signal, 5H, B–H), 1.12 (broad signal, 5H, B–H), 1.06 (broad signal, 1H, B–H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 23 °C): δ 161.9 (N=C–N), 134.6, 134.2, 129.8, 129.2 (4 aryl signals), 56.9, 44.8, 40.0. $^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN, 23 °C): δ −6.9 (1B, B–N), −13.0 to −18.0 (overlapping signals with peaks at −15.2 and −16.1 ppm, 11B, B–H). High-resolution ESI-MS (negative mode, MeOH): m/z calcd for $[C_{11}H_{27}B_{12}Cl_2N_3–H]^-$: 400.2699. Found: 400.2714.

Synthesis of urea [NBu_4]$_2$(**7a**): In a glovebox filled with N_2, a 20 mL vial was charged with $[Et_3NH][B_{12}H_{11}NH_3]$ (260 mg, 1.00 mmol, 1 equiv), NaH (53 mg, 2.2 mmol, 2.2 equiv) and a stir bar. THF (10 mL) was added, and the mixture was stirred at room temperature for 10 min until there was no H_2 evolution anymore. Phenyl isocyanate (238 mg, 2.0 mmol, 2 equiv) was slowly added. The conversion was complete after stirring for 5 h. The flask was transferred out of the glovebox. The solvent was removed under vacuum, and H_2O (10 mL) was added. The aqueous solution was heated to 50 °C, and $[NBu_4]Br$ (677 mg, 2.1 mmol, 2.1 equiv) was added. A white solid precipitated immediately and was collected by filtration. It was dried under vacuum overnight to afford $[NBu_4]_2$[**7a**] as a colorless microcrystalline product (685 mg, 90%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.52 (broad s, 1H, anionic NH), 7.41 (d, 2H, J = 8.2 Hz, Ph H), 7.18 (dd, 2H, J = 8.2 Hz, 7.6 Hz, Ph–H), 6.83 (t,1H, J = 7.6 Hz, Ph–H), 3.96 (broad s, 1H, NH), 3.25–3.01 (m, 16H, cationic N–CH_2), 1.67-1.50 (m, 16H, cationic N-CH_2CH_2), 1.41–1.27 (overlapping m and s, 21H, cationic N–$CH_2CH_2CH_2$ and B–H), 1.04 (s, 5H, B–H), 0.95 (t, 24H, J = 7.3 Hz, cationic CH_3), 0.85 (s, 1H, B–H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 158.6, 142.8, 129.5 (overlapping signals), 121.2, 59.2, 24.3, 20.3, 10.8. $^{11}B\{^1H\}$ NMR (128 MHz,

CD_3CN): δ = –5.0 (1B, B–N), –15.4 (5B, B–H), –16.2 (5B, B–H), –19.3 (1B, B–H). High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_7H_{18}B_{12}N_2O]^{2-}$ 138.1320. Found: 138.1331.

Synthesis of urea $[PPh_4]_2$(**7b**): This product was prepared in a similar manner to $[NBu_4]_2$[**7a**], using 4-chlorophenyl isocyanate (307 mg, 2.0 mmol, 2 equiv) and $[PPh_4]Br$ (881 mg, 2.1 mmol, 2.1 equiv). $[PPh_4]_2$[**7b**] was obtained as a colorless microcrystalline solid (869 mg, 91%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.59 (s, 1H, anionic NH), 7.95-7.85 (m, 8H, cationic H), 7.81–5.58 (overlapping m, 32H, cationic H), 7.41–7.28 (m, 2H, Ph–H), 7.13–6.96 (m, 2H, Ph–H), 4.00 (s, 1H, N–H), 1.33 (broad signal, 5H, B–H), 1.07 (broad signal, 5H, B–H), 0.88 (broad signal, 1H, B–H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 158.4, 141.7, 136.4 (d, $J_{P,C}$ = 2.4 Hz, cation CH), 135.6 (d, $J_{P,C}$ = 10 Hz, cation CH), 131.3 (d, $J_{P,C}$ =13.0 Hz, cation CH), 129.2, 124.9, 119.6, 118.8 (d, $J_{P,C}$ = 89 Hz, cation C_q). $^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = −5.0 (1B, B–N), −15.5 (5B, B–H), −16.2 (5B, B-H), −19.2 (1B, B–H). High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_7H_{17}B_{12}N_2OCl]^{2-}$ 155.1125. Found: 155.1133.

Synthesis of isocyanate $[MePPh_3]_2$(**8**): In a glovebox filled with N_2, a 50 mL round-bottom flask was charged with $Cs[B_{12}H_{11}NH_3]$ (594 mg, 2.0 mmol, 1 equiv), NaH (144 mg, 6.0 mmol, 3 equiv) and a stir bar. DMF (10 mL) was added, and the mixture was stirred at 25 °C for 10 min until there was no H_2 evolution anymore. Then $ClC(O)NMe_2$ (6 equiv) diluted in DMF (2 mL) was slowly added by an Eppendorf pipet. The conversion was complete after stirring for 4 h. The flask was transferred out of the glovebox, and the volatiles were removed under vacuum. The residue was dissolved in H_2O (10 mL) at *ca.* 90 °C, giving a slightly yellow solution. The solution was stirred at 80–100 °C for 1 h, and $[MePPh_3]Br$ (1.29 g, 5 mmol, 2.5 equiv) was added. A white precipitate formed, and it was was collected by filtration. Purification by column chromatography (eluent DCM/MeCN 4:3) afforded $[MePPh_3]_2$[8] as a colorless solid (369 mg, 25%). $^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 7.90–7.83 (m, 6H, cationic CH), 7.76–7.62 (overlapping m, 24H, cationic CH), 2.83 (d, *J* = 13.8 Hz, 6H, CH_3), 1.23 (broad signal, 5H, B–H), 0.97 (broad signal, 5H, B-H), 0.75 (broad signal, 1H, B–H). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 136.1 (d, $J_{P,C}$= 3.0 Hz, cation CH), 134.2 (d, $J_{P,C}$= 11 Hz, cation CH), 131.1 (d, $J_{P,C}$= 13 Hz, cation CH), 120.4 (d, $J_{P,C}$= 89 Hz, cation C_q), 9.37 (d, $^1J_{P,C}$= 58 Hz, cation CH_3). The N=C=O carbon atom could not be detected unambiguously. $^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = −7.74 (1B, B–N), −15.4 (5B, B–H), −16.7 (5B, B–H), −19.6 (1B, B–H). Mass-spectrometric characterization of this product proved difficult; the results that were obtained by negative-mode ESI-MS are shown in Figure S2, along with the IR spectrum in Figure S3.

Additional figures, X-ray crystallographic data and copies of NMR spectra are provided in the Supporting Information file; see "Supplementary Materials".

4. Conclusions

In summary, the synthesis and characterization of a series of compounds based on the amino-dodecaborate anion **2** has been achieved, including amidinium ions **6**, amides **3**, ureas **7** and dodecaboranyl isocyanate **8**. The new products have been fully characterized spectroscopically, and solid-state structures have been elucidated for nine derivatives. Amidinium ions **7** are reported for the first time, as well as aromatic ureas of the structure $\{B_{12}\}$NH-C(O)-NHAr. A facile method for the interconversion of the dianionic and monoanionic form of amides **3** has been developed, which is of relevance in view their different physical properties, in particular solubility and crystallinity. A fragmentation-based approach to dodecaboranyl isocyanate **8** was developed, which is expected to provide access to novel $\{B_{12}\}$ derivatives by subsequent nucleophilic addition to the NCO group or by pericyclic reactions. The transformations leading to **6**, **7** and **8** extend the synthetic toolbox to produce boron clusters for applications in various areas.

Supplementary Materials: The following are available online: Supporting Information file with experimental procedures and spectroscopic data. Crystal structures have been deposited with the Cambridge Crystallographic Data Centre: CCDC1861483–1861492. They are available free of charge from www.ccdc.cam.ac.uk.

Author Contributions: Y.Z. and Y.S. carried out the majority of the synthetic work and contributed equally; T.W. conducted additional experiments; J.L. and B.S. solved the X-ray crystal structures; Y.Z. and S.D. wrote the manuscript; S.D. supervised the study.

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Sample Availability: Not available.

Supplementary Information for

Synthesis and X-ray structural characterization of amidine, amide, urea and isocyanate derivatives of the *closo*-aminododecaborate anion $[B_{12}H_{11}(NH_3)]^-$

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I General Information

Chemicals

If not otherwise specified, reagents and organic solvents were commercially available and used without further purification. Anhydrous solvents were prepared by passage through activated Al_2O_3 and stored over 3 Å molecular sieves. CD_3CN and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories and filtered through Al_2O_3 prior to use. $[B_{12}H_{12}]^{2-}$ and $[B_{12}H_{11}NH_3]^-$ salts and dodecaborate amides **3a**–**e** were prepared according to the literature.[1–3]

Reaction Conditions

Glassware for air-sensitive reations was dried at 150 °C and allowed to cool in a vacuum. Reactions carried out in a glovebox were run under a nitrogen atmosphere with O_2, H_2O <1 ppm.

Characterization

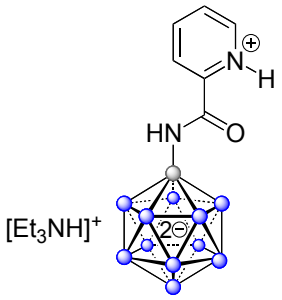
Thin-layer chromatography (TLC) was carried out using silica gel 60, F254 with a thickness of 0.25 mm. Column chromatography was performed on silica gel 60 (200-30 mesh).

Low-resolution ESI-MS data were recorded on Advion Expression CMS instrument. High-resolution MS data were recorded using IT-TOF detection (Shimadzu, Japan) equipped with an electrospray ionization source (ESI). Accurate mass determination was corrected by calibration using sodium trifluoroacetate clusters as a reference.

Single-crystal X-ray diffraction studies were performed on an Oxford Diffraction Gemini A Ultra diffractometer equipped with an 135mm Atlas CCD detector and using Mo K-α radiation

NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer (^{1}H NMR 500.13 MHz, ^{13}C NMR 125.77 MHz, ^{11}B NMR 160.46 MHz) or a Bruker AVANCE III 400 spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, ^{11}B NMR 128.38 MHz) at the temperature indicated. Data are reported as follows: Chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc.), coupling constant *J* in Hz, integration, and (where applicable) interpretation. Signals were referenced against solvent peaks (^{1}H: residual $CHD_2C(O)CD_3$ = 2.05 ppm, residual CHD_2CN = 1.94 ppm, residual $CHDCl_2$ = 5.32 ppm, $^{13}C\{^{1}H\}$: $CD_3C(O)CD_3$ = 29.84 ppm, CD_3CN = 1.32 ppm, CD_2Cl_2 = 53.32 ppm). ^{11}B and $^{11}B\{^{1}H\}$ NMR spectra were calibrated against external BF_3*Et_2O = 0 ppm (BF_3*Et_2O capillary in C_6D_6).

II Experimental Section



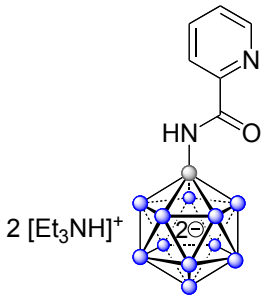
Synthesis of [Et$_3$NH][3e-H]: In a glovebox filled with N_2, a 20 mL vial was charged with [Et$_3$NH][$B_{12}H_{11}NH_3$] (212.4 mg, 0.817 mmol, 1 equiv), NaH (138.2 mg, 5.758 mmol, 7 equiv) and a stir bar. THF (4 mL) and DMF (4 mL) were added, and the mixture was stirred at room temperature for 10 minutes until there was no H_2 evolution anymore. Then pyridine-2-carbonyl chloride hydrochloride PyCOCl·HCl (220.2 mg, 1.237 mmol, 1.5 equiv) was slowly added. The conversion was complete after stirring for 5 h. The flask was transferred out of the glovebox. H_2O (4 mL) was added, and the pH value of the reaction mixture was adjusted to 2–3 with 1 M aqueous HCl. [NEt$_3$H]Cl (300 mg, 2.180 mmol, 2.7 equiv) was added, and the reaction mixture was extracted with MeCN/EtOAc (1:2 *v*/*v*). The organic layers were concentrated on a rotary evaporator. The residue was purified by recrystallization from methanol to afford yellowish crystals of [Et$_3$NH][**3e-H**] (150 mg, 50%).

^{1}H{^{11}B} NMR (400 MHz, CD_3CN): δ = 8.96 (s, 1H, anionic N*H*), 8.90-8.86 (m, 1H, Py H), 8.18-8.14 (overlapping m, 2H, Py H), 7.89-7.72 (m, 1H, Py H), 6.63 (t,1H, J_{NH} = 52 Hz, N*H*), 3.27 (s, 1H, N*H*), 3.20-3.15 (m, 6H, cationic N-CH_2), 1.47 (broad signal, 5H, B-H), 1.24 (t, *J* = 7.4 Hz, 9H, cationic CH_3), 1.20 (broad signal, 5H, B-H), 1.13 (broad signal, 1H, B-H).

^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ = 166.7, 149.5, 143.9, 141.5, 129.8, 124.5 (6 anionic signals), 48.0, 9.2 (2 cationic signals).

^{11}B{^{1}H} NMR (128 MHz, CD_3CN): δ = -7.6 (1B, *B*-N), -15.3 (5B, *B*-H), -15.7 (overlapping signals, 6B, *B*-H).

High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_6H_{17}B_{12}N_2O]^-$ 263.2430. Found: 263.2459.



Transformation of [Et$_3$NH][3e-H] to [Et$_3$NH]$_2$[3e]: A 20 mL vial was charged with [Et$_3$NH][**3e-H**] (50 mg) and a stir bar. MeCN (3 mL) and Et$_3$N (0.5 mL) were added, and the solution was stirred at room temperature for 1 h. Then the stir bar was removed, and the solution was concentrated on a rotary evaporator and dried overnight under vacuum at 80 °C to afford compound [Et$_3$NH]$_2$[**3e**] in quantitative yield.

This method can also be applied for the transformation of other compounds **3-H** to **3** quantitatively. $^{11}B\{^1H\}$ NMR spectra of **3b**, **3b-H**, **3e** and **3e-H** are displayed in Figure S1.

$^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.56 (broad signal, 1H, Py H), 8.09-8.00 (m, 1H, Py H), 7.99-7.80 (overlapping m, 2H, Py H and amide N-H), 7.50-7.38 (m, 1H, Py H), 4.63 (broad t, 2H, J_{NH} = 52 Hz, N-H from cation), 3.25-3.01 (m, 12H, cationic N-CH_2), 1.34 (s, 5H, B-H), 1.24 (t, J = 7.4 Hz, 9H, cationic CH_3), 1.03 (broad signal, 5H, B-H), 0.89 (broad signal, 1H, B-H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 166.2, 152.9, 149.0, 138.5, 126.4, 122.2 (6 anionic signals), 47.8, 9.1 (2 cationic signals).

$^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = -5.3 (1B, B-N), -15.3 (5B, B-H), -16.4 (5B, B-H), -18.7 (1B, B-H).

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_6H_{17}B_{12}N_2O]^{2-}$ 131.1226. Found: 131.1254.

The $^{11}B\{^1H\}$ NMR spectra of **3b**, **3b-H**, **3e** and **3e-H** are shown in Figure S1 as representative examples to demonstrate the effect of protonation. For both product pairs **3b**/**3b-H** and **3e**/**3e-H**, similar effects are observed. Upon protonation, the B–N signal is shifted from –5 ppm to –8 ppm. On the other hand, the B–H vertices become more deshielded; the B12 signal appears at –19 ppm in the dianionic form and overlaps with the B2–11 resonances in the monoanionic form.

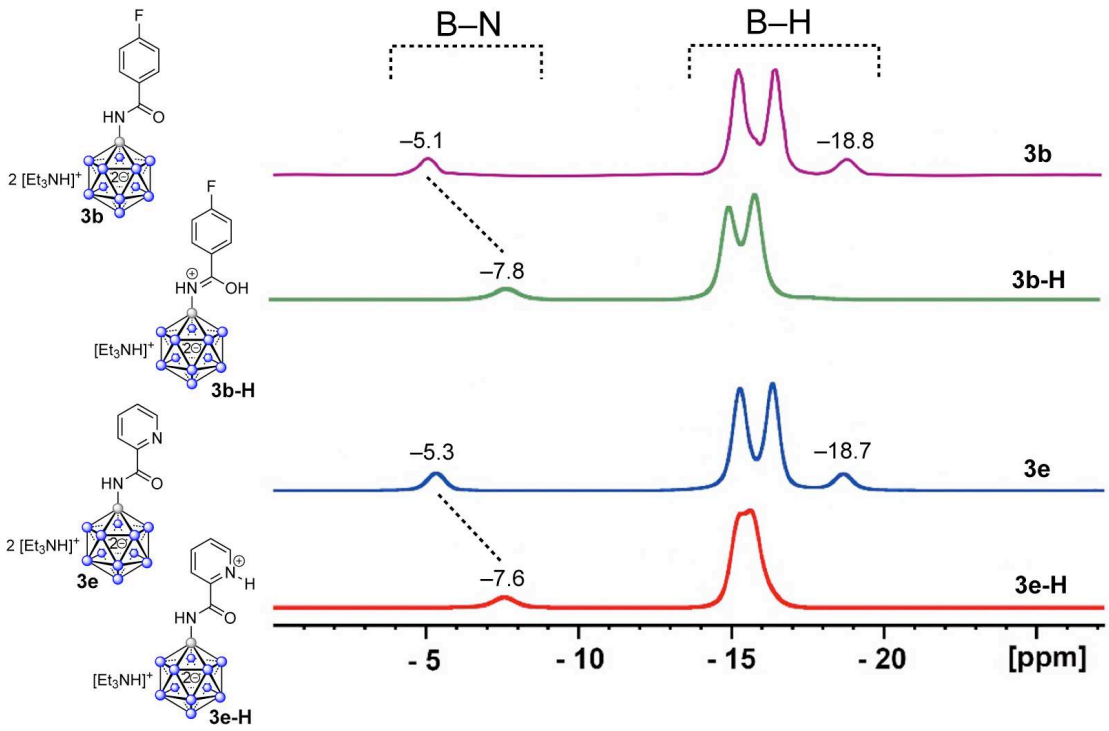
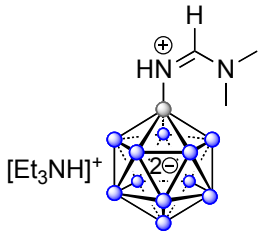


Figure S1. $^{11}B\{^1H\}$ NMR spectra of **3b**, **3b-H**, **3e** and **3e-H** (acetonitrile-d_3,128 MHz, 23 °C).



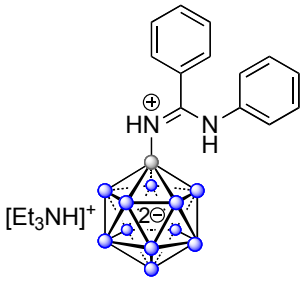
Synthesis of amidine [Et$_3$NH][6a]: In a glovebox, a dry 20 mL vial, equipped with a stir bar, was charged with [Et$_3$NH][B$_{12}$H$_{11}$NH$_3$] (102 mg, 0.40 mmol, 1 equiv). Then anhydrous DMF (1 mL) was added. The vial was transferred to a fumehood, and dry Et$_3$N (1.0 mL, 7.20 mmol, 18 equiv) was added to the solution under N_2 protection. Then 2,4,6-trimethylphenylcarboxylic acid chloride (110 mg, 0.60 mmol, 1.5 equiv) was added. The mixture was stirred at 25 °C for 4 h. The reaction was quenched with an aqueous [Et$_3$NH]Cl solution (2 mL H_2O + 2 equiv [Et$_3$NH]Cl); the pH value at this point was ca. 7–8. The mixture was extracted with DCM/MeCN = 4 : 1 (8 x 10 mL). The combined organic layers were dried over $MgSO_4$, and the solution was filtered and concentrated by rotary evaporation. The cloudy residue was purified by silica gel column chromatography (eluent DCM/MeCN = 10:3, fraction size 20 mL). The combined eluates were concentrated on a rotary evaporator and dried under vacuum at 60 °C overnight to afford compound [Et$_3$NH][**6a**] as a colorless solid (50.4 mg, 40%).

^{1}H{^{11}B} NMR (400 MHz, CD_3CN, 23 °C): δ 7.76 (d, *J* = 16.0 Hz, 1H, N=CH-N), 6.41 (broad signal, 1H, N-H), 3.13 (q, *J* = 7.2 Hz, 6H, cationic N-CH2), 3.08 (s, 3H, anionic N-CH_3), 2.83 (s, 3H, anionic N-CH_3), 1.26 (broad signal, 5H, B-H), 1.24 (t, *J* = 7.2 Hz, 9H, cationic N-$CH_2C\mathit{H}_3$), 1.03 (broad signal, 5H, B-H), 0.85 (broad signal, 1H, B-H).

^{13}C{^{1}H} NMR (100 MHz, CD_3CN, 23 °C): δ 157.3 (N=C-N), 48.0 (cationic CH_2), 43.1, 35.7 (two N-C signals), 9.2 (cationic CH_3).

^{11}B{^{1}H} NMR (160 MHz, CD_3CN, 23 °C): δ -4.2 (1B, B-N), -14.5 to -17.0 (10B, B-H), -19.0 (1B, B-H).

High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_3H_{19}B_{12}N_2]^-$: 213.2738. Found: 213.2762.



Synthesis of amidine [Et_3NH][6b]: A dry 20 mL vial, equipped with a stir bar, was charged with $[Et_3NH]_2[B_{12}H_{11}NHCOC_6H_5]$ (101 mg, 0.22 mmol, 1 equiv). Then anhydrous MeCN (3 mL) was added, and dry Et_3N (0.3 mL, 2.16 mmol, 9.8 equiv) was added to the solution under N_2 protection. Pentafluorophenylcarboxylic acid chloride (80.0 mg, 0.35 mmol, 1.5 equiv) was added at 25 °C. The temperature was raised to 50 °C. After 30 min, aniline (61 mg, 0.66 mmol, 3.0 equiv) was added. The mixture was stirred for another 4 h and concentrated by rotary evaporation. The cloudy residue was purified by silica gel column chromatography (eluent DCM/MeCN = 4:1, fraction size 20 mL). The combined eluates were concentrated on a rotary evaporator and dried under vacuum at 60 °C overnight to afford compound [Et_3NH][**6b**] as a yellow solid (87.7 mg, 91%).

$^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2, 23 °C): δ 10.00 (s, 1H, N-H), 7.53-7.48 (m, 1H, phenyl H), 7.41-7.35 (overlapping m, 4H, phenyl H), 7.24-7.09 (overlapping m, 3H, phenyl H), 7.03-6.78 (overlapping broad signal and m, 3H, phenyl H and N-H), 6.65 (broad signal, 1H, N-H) 3.29-3.22 (m, 6H, cationic N-CH_2), 1.62 (broad signal, 5H, B-H), 1.40 (t, J = 7.2 Hz, 9H, cationic N-CH_2CH_3), 1.22 (broad signal, 5H, B-H), 1.05 (broad signal, 1H, B-H).

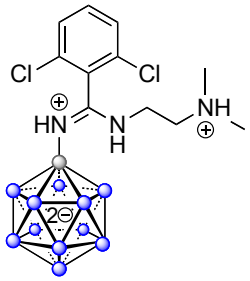
This spectrum contained small signals at 7.18, 6.71 and 6.67 ppm ascribed to residual aniline

$^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 23 °C): δ 165.6 (N=C-N), 138.1, 133.2, 131.3, 130.4, 130.1, 129.9, 127.5, 125.6 (8 aryl signals), 48.3 (cationic N-CH_2), 9.4 (cationic N-CH_3).

This spectrum showed small signals at 149.1, 130.2, 118.3 and 115.6 ppm ascribed to residual aniline.

$^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2, 23 °C): δ -5.8 (1B, B-N), -13.5 to -16.5 (10B, B-H), -17.4 (1B, B-H).

High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_{13}H_{23}B_{12}N_2]^-$: 337.3056. Found: 337.2382.



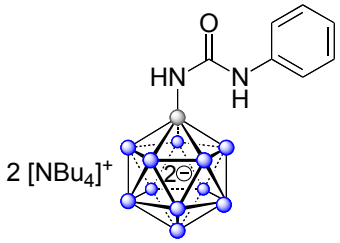
Synthesis of amidine [Et_3NH][6c]: A dry 20 mL vial, equipped with a stir bar, was charged with $[Et_3NH]_2[B_{12}H_{11}NHCOC_6H_3Cl_2]$ (177 mg, 0.33 mmol, 1 equiv). Then anhydrous MeCN (3 mL) was added, and dry Et_3N (0.45 mL, 3.25 mmol, 9.8 equiv) was added to the solution under N_2 protection. Pentafluorophenylcarboxylic acid chloride (128 mg, 0.55 mmol, 1.7 equiv) was added at 25 °C. The temperature was raised to 50 °C. After 30 min, *N,N*-dimethylethylamine (88 mg, 1.00 mmol, 3.0 equiv) was added. The mixture was stirred for another 4 h, and 1 M aqueous HCl (5 mL) was added. The suspension was extracted with EtOAc/MeCN 3:1 (5 x 10 mL). The combined organic layers were dried over $MgSO_4$, and the solution was filtered and concentrated by rotary evaporation. The cloudy residue was purified by silica gel column chromatography (eluent DCM/MeCN = 4:3, fraction size 20 mL). The combined eluates were concentrated and dried under vacuum at 60 °C overnight to afford compound [Et_3NH][**6c**] as a yellow solid (132 mg, 100%).

$^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN, 23 °C): δ 8.54 (broad signal, 1H, N-H), 7.59-7.55 (overlapping m, 3H, aryl H), 7.46 (broad signal, 1H, N-H), 6.98 (very broad signal, 1H, N-H), 3.43 (dt, *J* = 7.2 Hz, 7.2 Hz, 2H, CH_2), 3.24 (t, *J* = 7.2 Hz, 2H, CH_2), 2.77 (s, 6H, N-CH_3), 1.41 (broad signal, 5H, B-H), 1.12 (broad signal, 5H, B-H), 1.06 (broad signal, 1H, B-H).

$^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN, 23 °C): δ 161.9 (N=C-N), 134.6, 134.2, 129.8, 129.2 (4 aryl signals), 56.9, 44.8, 40.0.

$^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN, 23 °C): δ -6.9 (1B, B-N), -13.0 to -18.0 (overlapping signals with peaks at -15.2 and -16-1 ppm, 11B, B-H).

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_{11}H_{27}B_{12}Cl_2N_3\text{-}H]^-$: 400.2699. Found: 400.2714.



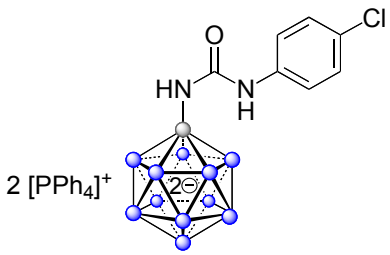
Synthesis of urea [NBu$_4$]$_2$[7a]: In a glovebox filled with N_2, a 20 mL vial was charged with [Et$_3$NH][$B_{12}H_{11}NH_3$] (260 mg, 1.00 mmol, 1 equiv), NaH (53 mg, 2.2 mmol, 2.2 equiv) and a stir bar. THF (10 mL) was added, and the mixture was stirred at room temperature for 10 minutes until there was no H_2 evolution anymore. Phenyl isocyanate (238 mg, 2.0 mmol, 2 equiv) was slowly added. The conversion was complete after stirring for 5 h. The flask was transferred out of the glovebox. The solvent was removed under vacuum, and H_2O (10 mL) was added. The aqueous solution was heated to 50 °C, and [NBu$_4$]Br (677 mg, 2.1 mmol, 2.1 equiv) was added. A white solid precipitated immediately and was collected by filtration. It was dried under vacuum overnight to afford [NBu$_4$]$_2$[**7a**] as a colorless microcrystalline product (685 mg, 90%).

$^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.52 (broad s, 1H, anionic NH), 7.41 (d, 2H, *J* = 8.2 Hz, Ph H), 7.18 (dd, 2H, *J* = 8.2 Hz, 7.6 Hz, Ph *H*), 6.83 (t,1H, *J* = 7.6 Hz, Ph *H*), 3.96 (broad s, 1H, N*H*), 3.25-3.01 (m, 16H, cationic N-CH_2), 1.67-1.50 (m, 16H, cationic N-CH$_2$CH_2), 1.41-1.27 (overlapping m and s, 21H, cationic N-CH$_2$CH$_2$CH_2 and B-*H*), 1.04 (s, 5H, B-H), 0.95 (t, 24H, *J* = 7.3 Hz, cationic CH_3), 0.85 (s, 1H, B-H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 158.6, 142.8, 129.5 (overlapping signals), 121.2, 59.2, 24.3, 20.3, 10.8.

$^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = -5.0 (1B, B-N), -15.4 (5B, B-H), -16.2 (5B, B-H), -19.3 (1B, B-H).

High-resolution ESI-MS (negative mode, MeOH): *m/z* calcd for $[C_7H_{18}B_{12}N_2O]^2$ 138.1320. Found: 138.1331.



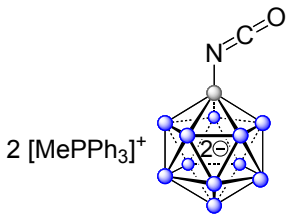
Synthesis of urea $[PPh_4]_2$[7b]: This product was prepared in a similar manner to $[NBu_4]_2$[**7a**], using 4-chlorophenyl isocyanate (307 mg, 2.0 mmol, 2 equiv) and $[PPh_4]Br$ (881 mg, 2.1 mmol, 2.1 equiv). $[PPh_4]_2$[**7b**] was obtained as a colorless microcrystalline solid (869 mg, 91%).

$^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 8.59 (s, 1H, anionic NH), 7.95-7.85 (m, 8H, cationic H), 7.81-5.58 (overlapping m, 32H, cationic H), 7.41-7.28 (m, 2H, Ph H), 7.13-6.96 (m, 2H, Ph H), 4.00 (s, 1H, N-H), 1.33 (broad signal, 5H, B-H), 1.07 (broad signal, 5H, B-H), 0.88 (broad signal, 1H, B-H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 158.4, 141.7, 136.4 (d, $J_{P,C}$ = 2.4 Hz, cation CH), 135.6 (d, $J_{P,C}$ = 10 Hz, cation CH), 131.3 (d, $J_{P,C}$ =13.0 Hz, cation CH), 129.2, 124.9, 119.6, 118.8 (d, $J_{P,C}$ = 89 Hz, cation C_q).

$^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = -5.0 (1B, B-N), -15.5 (5B, B-H), -16.2 (5B, B-H), -19.2 (1B, B-H).

High-resolution ESI-MS (negative mode, MeOH): *m*/*z* calcd for $[C_7H_{17}B_{12}N_2OCl]^{2-}$ 155.1125. Found: 155.1133.



Synthesis of isocyanate [MePPh$_3$]$_2$[8]: In a glovebox filled with N_2, a 50 mL round-bottom flask was charged with Cs[$B_{12}H_{11}NH_3$] (594 mg, 2.0 mmol, 1 equiv), NaH (144 mg, 6.0 mmol, 3 equiv) and a stir bar. DMF (10 mL) was added, and the mixture was stirred at 25 °C for 10 minutes until there was no H_2 evolution anymore. Then ClC(O)NMe_2 (6 equiv) diluted in DMF (2 mL) was slowly added by an Eppendorf pipet. The conversion was complete after stirring for 4 h. The flask was transferred out of the glovebox, and the volatiles were removed under vacuum. The residue was dissolved in H_2O (10 mL) at *ca.* 90 °C, giving a slightly yellow solution. The solution was stirred at 80–100 °C for 1 h, and [$MePPh_3$]Br (1.29 g, 5 mmol, 2.5 equiv) was added. A white precipitate formed, and it was was collected by filtration. Purification by column chromatography (eluent DCM/MeCN 4:3) afforded [$MePPh_3$]$_2$[**8**] as a colorless solid (369 mg, 25%).

$^1H\{^{11}B\}$ NMR (400 MHz, CD_3CN): δ = 7.90-7.83 (m, 6H, cationic CH), 7.76-7.62 (overlapping m, 24H, cationic CH), 2.83 (d, J = 13.8 Hz, 6H, CH_3), 1.23 (broad signal, 5H, B-H), 0.97 (broad signal, 5H, B-H), 0.75 (broad signal, 1H, B-H).

$^{13}C\{^1H\}$ NMR (101 MHz, CD_3CN): δ = 136.1 (d, $J_{P,C}$= 3.0 Hz, cation CH), 134.2 (d, $J_{P,C}$= 11 Hz, cation CH), 131.1 (d, $J_{P,C}$= 13 Hz, cation CH), 120.4 (d, $J_{P,C}$= 89 Hz, cation C_q), 9.37 (d, $^1J_{P,C}$= 58 Hz, cation CH_3). The N=C=O carbon atom could not be detected unambiguously.

$^{11}B\{^1H\}$ NMR (128 MHz, CD_3CN): δ = -7.74 (1B, B-N), -15.4 (5B, B-H), -16.7 (5B, B-H), -19.6 (1B, B-H).

Mass-spectrometric characterization of this product proved difficult; the results that were obtained by negative-mode ESI-MS are shown in Figure S2, along with the IR spectrum in Figure S3.

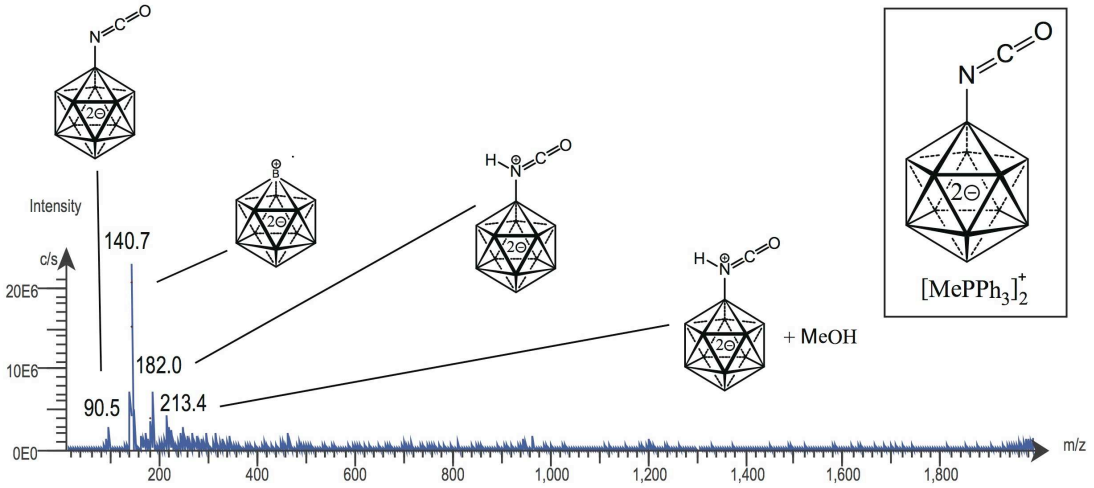


Figure S2. (–)-ESI Mass spectrum of **8** in MeOH.

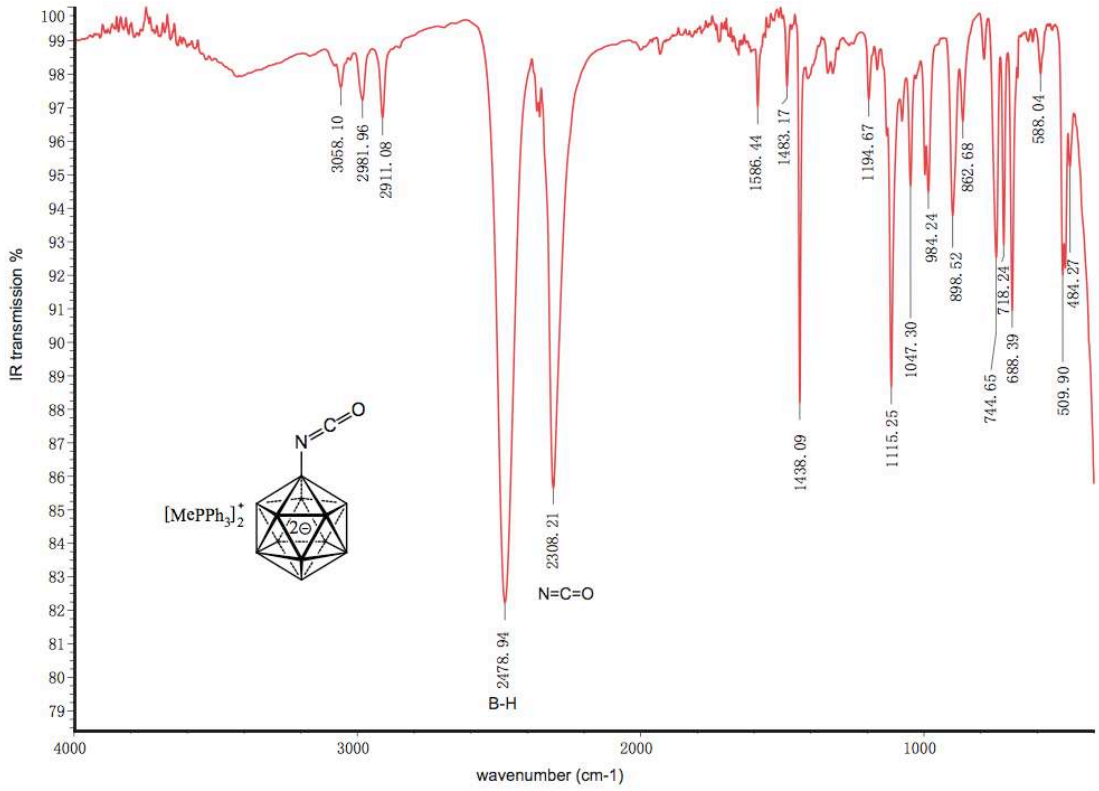


Figure S3. IR spectrum of $[PPh_4]_2$[**8**].

III X-ray Crystallography

CCDC1861483–1861492 contain the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystals of the products $[Et_3NH]_2$[**3b**], $[Et_3NH]$[**3d-H**], $[Et_3NH]_2$[**3e**], $[Et_3NH]$[**3e-H**], $[MePPh_3]$[**6a**], $[Et_3NH]$[**6c**] and $[MePPh_3]_2$[**8**] were measured at room temperature because the X-ray facility of our department does not routinely offer measurements with nitrogen cooling.

Crystal structure of $[Et_3NH]_2$[3a] (CCDC1861488)

Compound $[Et_3NH]_2$[**3a**] (20 mg) was dissolved in acetone/MeCN (0.25 mL/0.25 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long NMR tube and layered with hexanes (1 mL). Colorless crystals of the composition $[Et_3NH]_4[B_{12}H_{11}NHCOPh]_2 \cdot H_2O$ suitable for X-ray diffraction grew within 3 d at 25 °C.

Bond precision: C-C = 0.0084 A Wavelength=0.71073

Cell: a=10.3802(8) b=15.9133(12) c=18.0577(15)
alpha=79.497(7) beta=87.786(7) gamma=87.828(6)
Temperature: 170 K

	Calculated	Reported
Volume	2929.2(4)	2929.2(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C7 H17 B12 N O), 4(C6 H16 N), H2 O	2(C7 H17 B12 N O), 4(C6 H16 N), H2 O
Sum formula	C38 H100 B24 N6 O3	C38 H100 B24 N6 O3
Mr	948.68	948.67
Dx,g cm-3	1.076	1.076
Z	2	2
Mu (mm-1)	0.060	0.060
F000	1028.0	1028.0
F000'	1028.24	
h,k,lmax	12,19,21	12,19,21
Nref	10756	10623
Tmin,Tmax	0.972,0.977	0.849,1.000
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.849 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.988 Theta(max)= 25.350

R(reflections)= 0.1239(6692) wR2(reflections)= 0.3535(10623)

S = 1.034 Npar= 655

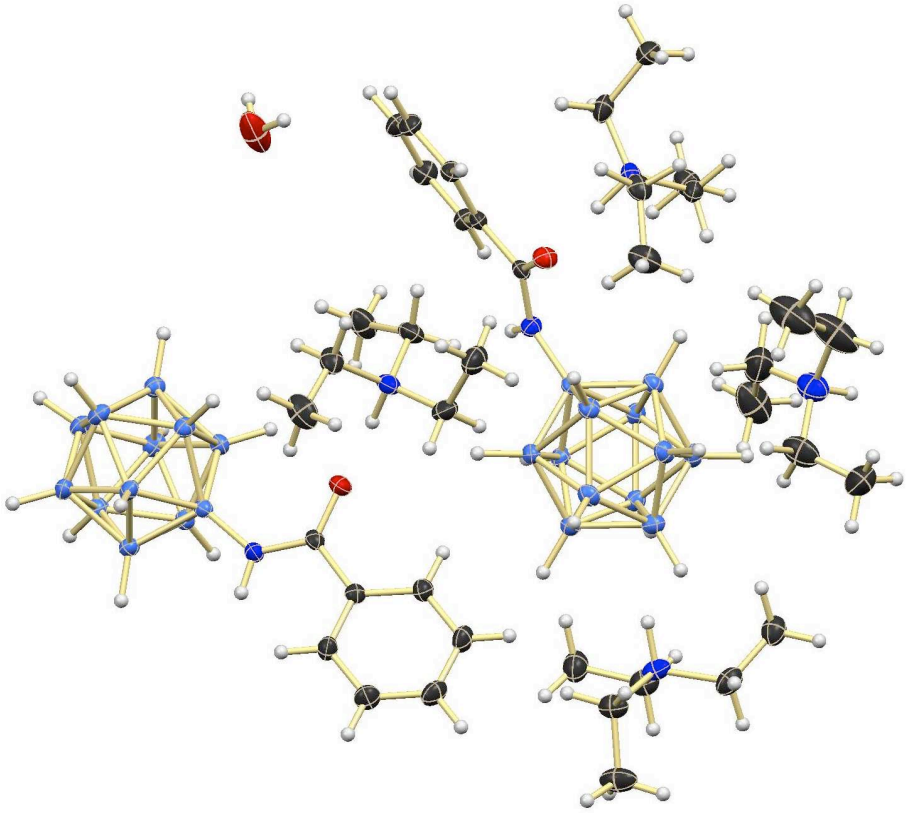


Figure S4. ORTEP representation of $[Et_3NH]_4[B_{12}H_{11}NHCOPh]_2 \cdot H_2O$; 30% displacement ellipsoids.

Crystal structure of $[Et_3NH]_2$[3b] (CCDC1861489)

Compound $[Et_3NH]_2$[**3b**] (20 mg) was dissolved in acetone/MeCN (0.25 mL/0.25 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long NMR tube and layered with hexanes (1 mL). Colorless crystals of the composition $[Et_3NH]_2[B_{12}H_{11}NHCO\text{-}C_6H_4\text{-}F]\cdot 0.5CH_3C(O)CH_3$ suitable for X-ray diffraction grew within 1 d at 25 °C.

Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=17.517(2) b=10.7703(8) c=35.537(4)
alpha=90 beta=106.010(11) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	6444.5(12)	6444.4(12)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	2(C7 H16 B12 F N O), 4(C6 H16 N), C3 H6 O	2(C7 H16 B12 F N O), C3 H6 O, 4(C6 H16 N)
Sum formula	C41 H102 B24 F2 N6 O3	C41 H102 B24 F2 N6 O3
Mr	1024.73	1024.72
Dx,g cm-3	1.056	1.056
Z	4	4
Mu (mm-1)	0.063	0.063
F000	2208.0	2208.0
F000'	2208.65	
h,k,lmax	21,12,42	21,12,42
Nref	5906	5882
Tmin,Tmax	0.973,0.992	0.780,1.000
Tmin'	0.970	

Correction method= # Reported T Limits: Tmin=0.780 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 25.350

R(reflections)= 0.0819(3329) wR2(reflections)= 0.2399(5882)

S = 1.015 Npar= 351

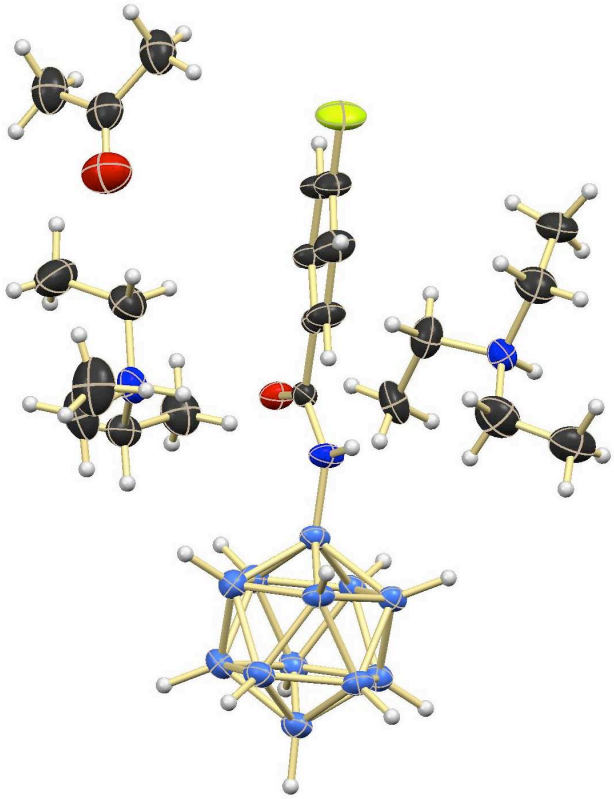


Figure S5. ORTEP representation of $[Et_3NH]_4[B_{12}H_{11}NHCO\text{-}C_6H_4\text{-}F]_2 \cdot CH_3C(O)CH_3$; 30% displacement ellipsoids.

Crystal structure of $[Et_3NH]_2$[3c] (CCDC1861486)

Compound $[Et_3NH]_2$[**3c**] (20 mg) was dissolved in MeCN (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long NMR tube and layered with Et_2O (1 mL). Colorless crystals of the composition $[Et_3NH]_2$ $[B_{12}H_{11}NHCO\text{-}C_6H_4\text{-}I]$ suitable for X-ray diffraction grew within 1 d at 25 °C.

Bond precision: C-C = 0.0060 A Wavelength=0.71073

Cell: a=10.4220(6) b=14.6666(8) c=20.0458(10)
alpha=90 beta=96.507(5) gamma=90
Temperature: 181 K

	Calculated	Reported
Volume	3044.4(3)	3044.4(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C7 H16 B12 I N O, 2(C6 H16 N)	C7 H16 B12 I N O, 2(C6 H16 N)
Sum formula	C19 H48 B12 I N3 O	C19 H48 B12 I N3 O
Mr	591.22	591.22
Dx,g cm-3	1.290	1.290
Z	4	4
Mu (mm-1)	1.071	1.071
F000	1216.0	1216.0
F000'	1214.35	
h,k,lmax	14,20,27	14,20,27
Nref	8520	7186
Tmin,Tmax	0.705,0.807	0.838,1.000
Tmin'	0.681	

Correction method= # Reported T Limits: Tmin=0.838 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.843 Theta(max)= 29.551

R(reflections)= 0.0530(5330) wR2(reflections)= 0.1254(7186)

S = 1.077 Npar= 331

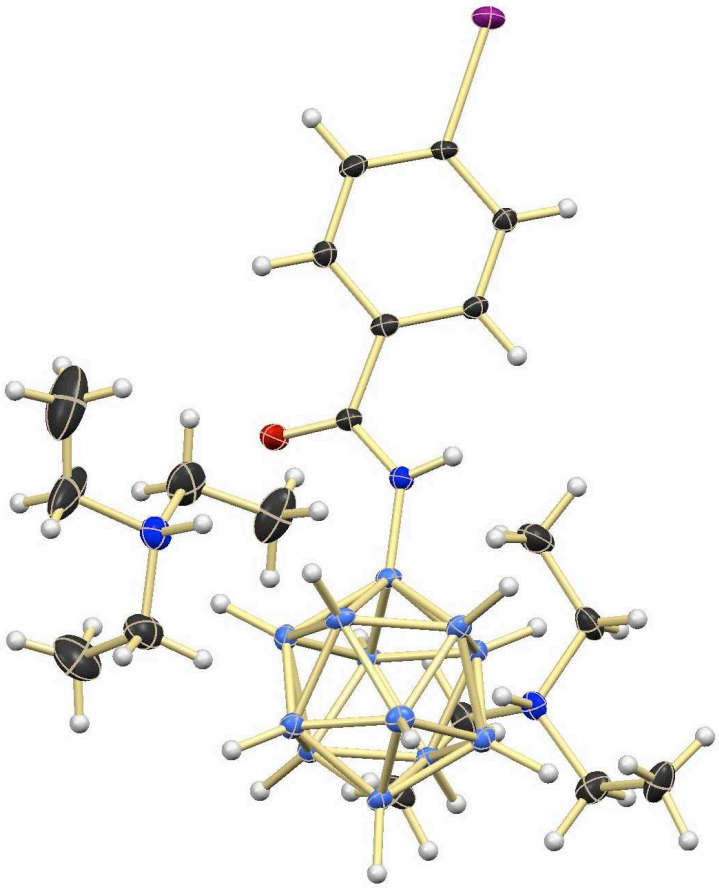


Figure S6. ORTEP representation of $[Et_3NH]_2[B_{12}H_{11}NHCO\text{-}C_6H_4\text{-}I]$; 30% displacement ellipsoids.

Crystal structure of [Et_3NH][3d-H] (CCDC1861491)

Compound [Et_3NH][**3d-H**] (10 mg) was dissolved in acetone (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into a 18 cm long NMR tube and layered with hexanes (1 mL). Colorless crystals of the composition [Et_3NH] [$B_{12}H_{11}NHC(OH)$-C_6H_4-OCH_3] suitable for X-ray diffraction grew within 5 d at 25 °C.

```
Bond precision:  B- B = 0.0051 A          Wavelength=0.71073

Cell:             a=9.0952(6)      b=35.086(2)      c=14.8327(9)
                  alpha=90         beta=90          gamma=90
Temperature:      293 K

                 Calculated                 Reported
Volume           4733.3(5)                  4733.4(5)
Space group      P c c n                    P c c n
Hall group       -P 2ab 2ac                 -P 2ab 2ac
Moiety formula   C8 H20 B12 N O2, C6 H16 N  C8 H20 B12 N O2, C6 H16 N
Sum formula      C14 H36 B12 N2 O2          C14 H36 B12 N2 O2
Mr               394.17                     394.17
Dx,g cm-3        1.106                      1.106
Z                8                          8
Mu (mm-1)        0.062                      0.062
F000             1680.0                     1680.0
F000'            1680.43
h,k,lmax         10,42,17                   10,42,17
Nref             4329                       4318
Tmin,Tmax        0.981,0.989                0.935,1.000
Tmin'            0.971

Correction method= # Reported T Limits: Tmin=0.935 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 25.349

R(reflections)= 0.0927( 2910)     wR2(reflections)= 0.3020( 4318)

S = 1.042                 Npar= 366
```

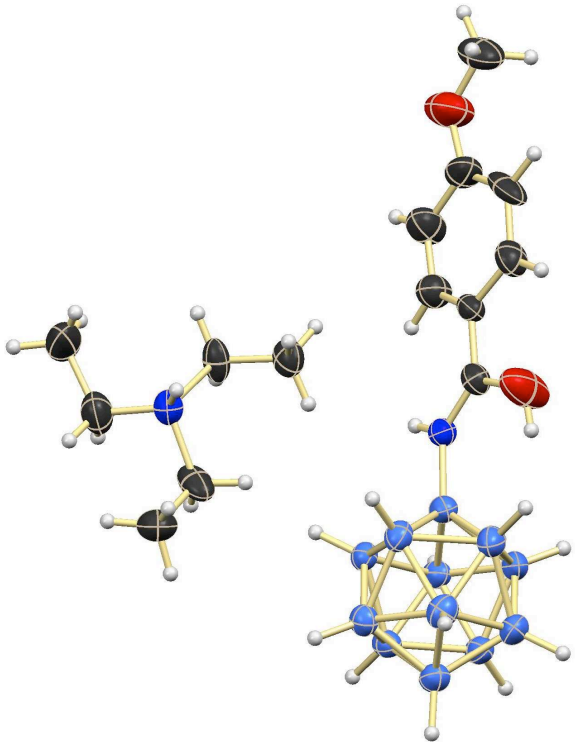


Figure S7. ORTEP representation of $[Et_3NH][B_{12}H_{11}NHC(OH)\text{-}C_6H_4\text{-}OCH_3]$; the protonated 4-methoxybenzamide moiety and the triethylammonium cation are both disordered. Only one of the two disordered parts is shown for clarity; 30% displacement ellipsoids.

Crystal structure of $[Et_3NH]_2$[3e] (CCDC1861492)

Compound $[Et_3NH]_2$[**3e**] (20 mg) was dissolved in MeCN (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long NMR tube and layered with Et_2O (1 mL). Colorless crystals of the composition $[Et_3NH]_2$ $[B_{12}H_{11}NHCO\text{-}C_5H_4N]$ suitable for X-ray diffraction grew within 2 d at 25 °C.

Bond precision: C-C = 0.0035 A Wavelength=0.71073

Cell: a=31.573(2) b=10.9139(7) c=17.2044(13)
alpha=90 beta=101.056(7) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	5818.3(7)	5818.3(7)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C6 H16 B12 N2 O, 2(C6 H16 N)	C6 H16 B12 N2 O, 2(C6 H16 N)
Sum formula	C18 H48 B12 N4 O	C18 H48 B12 N4 O
Mr	466.32	466.32
Dx,g cm-3	1.065	1.065
Z	8	8
Mu (mm-1)	0.059	0.059
F000	2016.0	2016.0
F000'	2016.43	
h,k,lmax	38,13,20	38,13,20
Nref	5345	5342
Tmin,Tmax	0.972,0.977	0.949,1.000
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.949 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 25.350

R(reflections)= 0.0605(3486) wR2(reflections)= 0.1775(5342)

S = 1.050 Npar= 350

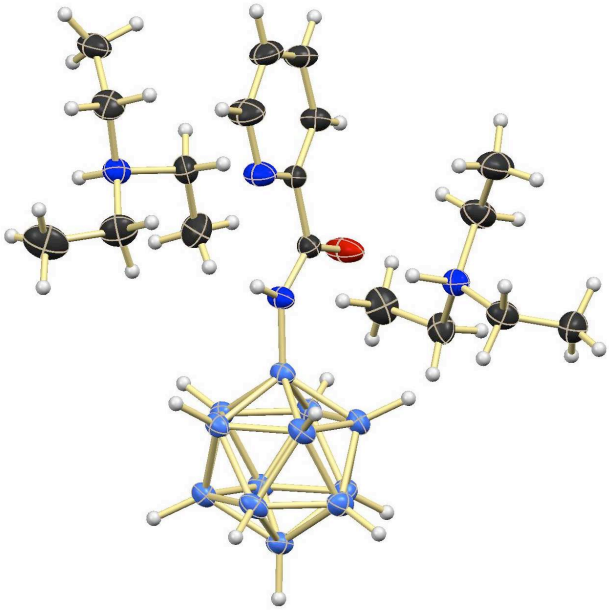


Figure S8. ORTEP representation of $[Et_3NH]_2[B_{12}H_{11}NHCO\text{-}C_5H_4N]$; 30% displacement ellipsoids.

Crystal structure of 3e-H (CCDC1861490)

Compound [Et_3NH][**3e-H**] (25 mg) was dissolved in MeOH/MeCN (1 mL/1 mL) at *ca.* 50 °C in a 4 mL glass vial and allowed to cool to room temperature. Colorless crystals of the composition [Et_3NH][$B_{12}H_{11}NHCO\text{-}C_5H_4N\text{-}H$]·$CH_3CN$ suitable for X-ray diffraction were obtained within 1 d.

Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=12.4068(12) b=15.2490(18) c=13.0624(12)
alpha=90 beta=102.374(10) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2413.9(4)	2413.9(4)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C6 H17 B12 N2 O, C6 H16 N, C2 H3 N	C6 H17 B12 N2 O, C6 H16 N, C2 H3 N
Sum formula	C14 H36 B12 N4 O	C14 H36 B12 N4 O
Mr	406.19	406.19
Dx,g cm-3	1.118	1.118
Z	4	4
Mu (mm-1)	0.062	0.062
F000	864.0	864.0
F000'	864.18	
h,k,lmax	14,18,15	14,18,15
Nref	4420	4405
Tmin,Tmax	0.976,0.982	0.948,1.000
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.948 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.348

R(reflections)= 0.0654(2790) wR2(reflections)= 0.1858(4405)

S = 1.025 Npar= 288

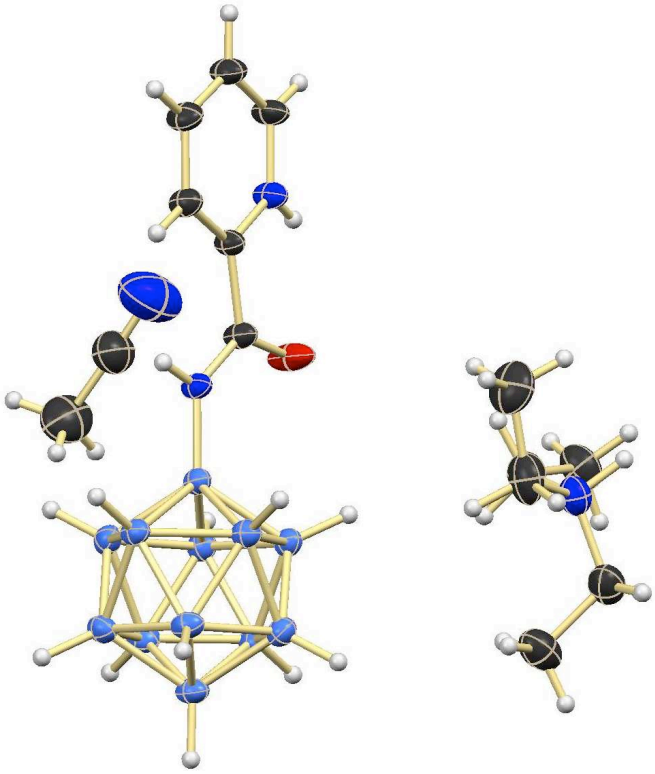


Figure S9. ORTEP representation of $[Et_3NH][B_{12}H_{11}NHCO\text{-}C_5H_4N\text{-}H]\cdot CH_3CN$; 30% displacement ellipsoids.

Crystal structure of [Et_3NH][6a] (CCDC1861483)

Compound [Et_3NH][**6a**] (10 mg, 0.031 mmol) was dissolved in acetonitrile (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into a 18 cm long NMR tube and layered with diethylether (1 mL). Colorless crystals of the composition $[Et_3NH][B_{12}H_{11}NH{=}CH{-}N(CH_3)_2]\cdot 2CH_3CN$ suitable for X-ray diffraction grew within 5 d at 25 °C.

Bond precision: C-C = 0.0028 A Wavelength=0.71073

Cell: a=8.7477(5) b=21.7928(15) c=13.5423(8)
alpha=90 beta=97.268(5) gamma=90

Temperature: 170 K

	Calculated	Reported
Volume	2560.9(3)	2560.9(3)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	C3 H19 B12 N2, C6 H16 N, 2(C2 H3 N)	C3 H19 B12 N2, C6 H16 N, 2(C2 H3 N)
Sum formula	C13 H41 B12 N5	C13 H41 B12 N5
Mr	397.23	397.23
Dx,g cm-3	1.030	1.030
Z	4	4
Mu (mm-1)	0.055	0.055
F000	856.0	856.0
F000'	856.13	
h,k,lmax	10,26,16	10,26,16
Nref	4700	4689
Tmin,Tmax	0.982,0.986	0.917,1.000
Tmin'	0.979	

Correction method= # Reported T Limits: Tmin=0.917 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.350

R(reflections)= 0.0464(3655) wR2(reflections)= 0.1289(4689)

S = 1.028 Npar= 278

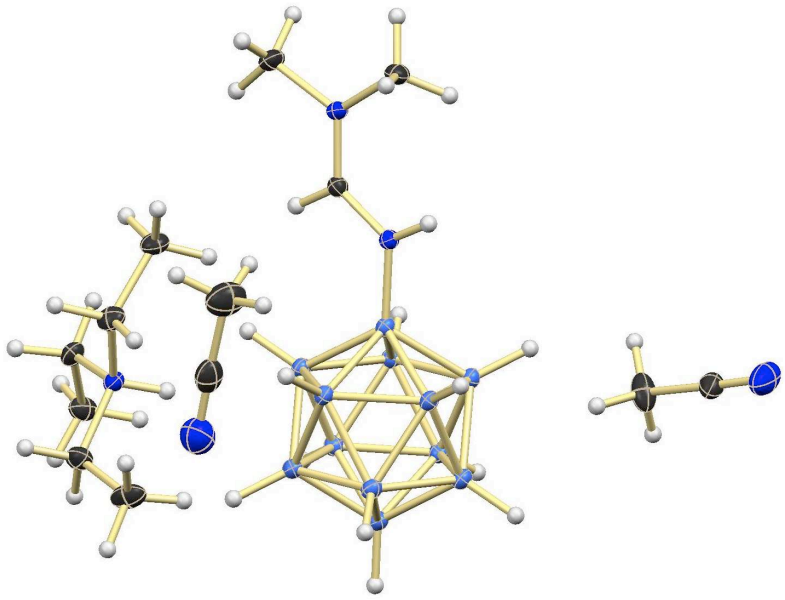


Figure S10. ORTEP representation of $[Et_3NH][B_{12}H_{11}NH{=}CH{-}N(CH_3)_2]\cdot 2CH_3CN$; 30% displacement ellipsoids.

Crystal structure of [$MePPh_3$][6a] (CCDC1861484)

Single crystals of **6a** were also obtained with the $[MePPh_3]^+$ cation, and the structure is similar to that of [Et_3NH][**6a**]. [Et_3NH][**6a**] (30 mg) was suspended in water (1 mL), and NaOH (2 equiv) was added to form the Na^+ salt. To this solution [$MePPh_3$]Br (2 equiv) was added to give [$MePPh_3$][**6a**] as a colorless precipitate. [$MePPh_3$][**6a**] (20 mg) was dissolved in acetone (0.5 mL). The resulting colorless solution was filtered into an 18 cm long NMR tube and layered with Et_2O (1 mL). Colorless crystals of the composition [$MePPh_3$] [$B_{12}H_{11}NH{=}CH{-}N(CH_3)_2$] suitable for X-ray diffraction grew within 2 d at 25 °C.

Bond precision: C-C = 0.0045 A Wavelength=0.71073

Cell: a=13.1538(7) b=20.5673(9) c=11.3688(6)
alpha=90 beta=103.263(5) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	2993.7(3)	2993.7(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H18 P, C3 H19 B12 N2	C19 H18 P, C3 H19 B12 N2
Sum formula	C22 H37 B12 N2 P	C22 H37 B12 N2 P
Mr	490.23	490.23
Dx,g cm-3	1.088	1.088
Z	4	4
Mu (mm-1)	0.108	0.108
F000	1032.0	1032.0
F000'	1032.62	
h,k,lmax	15,24,13	15,24,13
Nref	5485	5453
Tmin,Tmax	0.948,0.958	0.982,1.000
Tmin'	0.948	

Correction method= # Reported T Limits: Tmin=0.982 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 25.350

R(reflections)= 0.0587(3574) wR2(reflections)= 0.1595(5453)

S = 1.033 Npar= 337

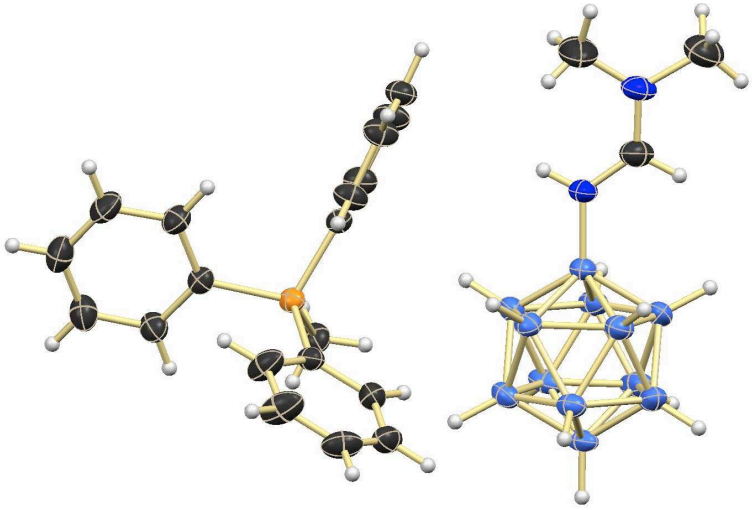


Figure S11. ORTEP representation of $[MePPh_3][B_{12}H_{11}NH{=}CH{-}N(CH_3)_2]$; 30% displacement ellipsoids.

Crystal structure of [Et_3NH][6c] (CCDC1861485)

Compound [Et_3NH][**6c**] (10 mg) was dissolved in acetonitrile (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into a 18 cm long NMR tube and layered with diethylether (1 mL). Colorless crystals of the composition [Et_3NH][$B_{12}H_{11}NH{=}C(C_6H_5)(NH\text{-}C_6H_5)$]·$H_2O$ suitable for X-ray diffraction grew within 5 d at 25 °C.

Bond precision: C-C = 0.0059 A Wavelength=0.71073

Cell: a=10.8688(7) b=12.0426(6) c=13.1037(9)
alpha=66.402(5) beta=67.187(6) gamma=85.080(5)
Temperature: 293 K

	Calculated	Reported
Volume	1443.85(18)	1443.85(15)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C13 H23 B12 N2, C6 H16 N, H2 O	C13 H23 B12 N2, C6 H16 N, H2 O
Sum formula	C19 H41 B12 N3 O	C19 H41 B12 N3 O
Mr	457.27	457.27
Dx,g cm-3	1.052	1.052
Z	2	2
Mu (mm-1)	0.057	0.057
F000	488.0	488.0
F000'	488.11	
h,k,lmax	13,14,15	13,14,15
Nref	5276	5202
Tmin,Tmax	0.976,0.980	0.985,1.000
Tmin'	0.976	

Correction method= # Reported T Limits: Tmin=0.985 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.986 Theta(max)= 25.350

R(reflections)= 0.0962(3419) wR2(reflections)= 0.3064(5202)

S = 1.050 Npar= 329

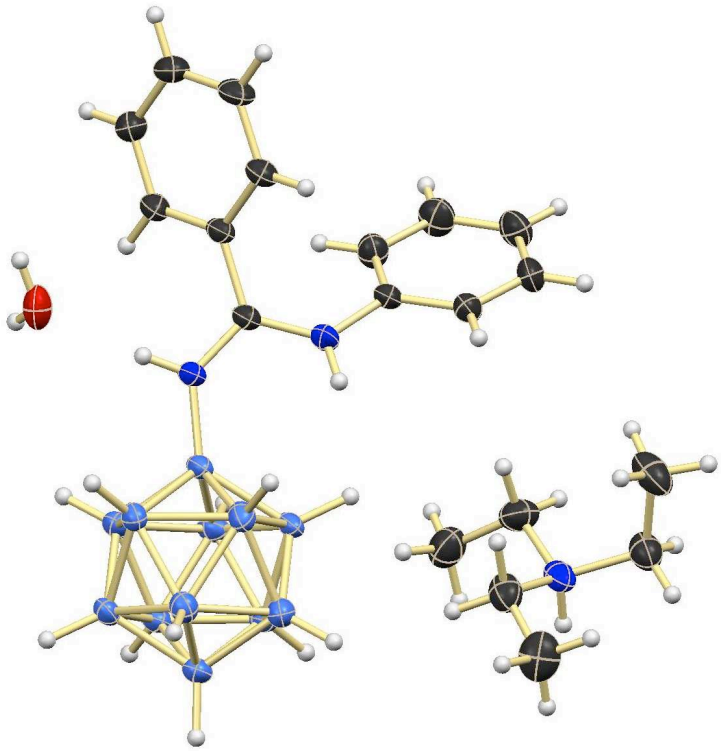


Figure S12. ORTEP representation of $[B_{12}H_{11}NH{=}C(C_6H_5)(NH\text{-}C_6H_5)]\cdot H_2O$; 30% displacement ellipsoids.

Crystal structure of $[MePPh_3]_2[8]$ (CCDC1861487)

$[MePPh_3]_2$[**8**] **(**10 mg) was dissolved in acetone (0.5 mL) in a 1 mL glass vial. The resulting colorless solution was filtered into an 18 cm long NMR tube and layered with Et_2O (1 mL). Colorless crystals of the composition $[MePPh_3]_2[B_{12}H_{11}N{=}C{=}O]$ suitable for X-ray diffraction grew within 2 d at 25 °C. Single crystals could also be obtained by recrystallization from aceotone.

Bond precision: C-C = 0.0041 A Wavelength=0.71073

Cell: a=11.3939(14) b=13.1505(15) c=14.8700(15)
alpha=89.844(9) beta=81.969(9) gamma=71.540(11)
Temperature: 293 K

	Calculated	Reported
Volume	2090.6(4)	2090.6(4)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	2(C19 H18 P), C H11 B12 N O	2(C19 H18 P), C H11 B12 N O
Sum formula	C39 H47 B12 N O P2	C39 H47 B12 N O P2
Mr	737.44	737.44
Dx,g cm-3	1.171	1.171
Z	2	2
Mu (mm-1)	0.137	0.137
F000	772.0	772.0
F000'	772.62	
h,k,lmax	13,15,17	13,15,17
Nref	7655	7633
Tmin,Tmax	0.952,0.973	0.575,1.000
Tmin'	0.952	

Correction method= # Reported T Limits: Tmin=0.575 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 25.350

R(reflections)= 0.0507(4888) wR2(reflections)= 0.1366(7633)

S = 0.961 Npar= 498

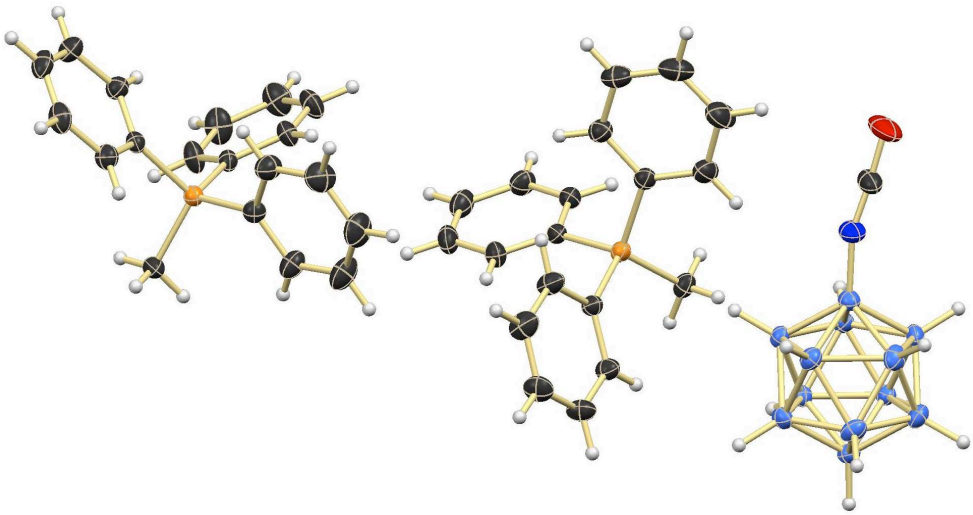


Figure S13. ORTEP representation of $[MePPh_3]_2[B_{12}H_{11}N{=}C{=}O]$; 30% displacement ellipsoids.

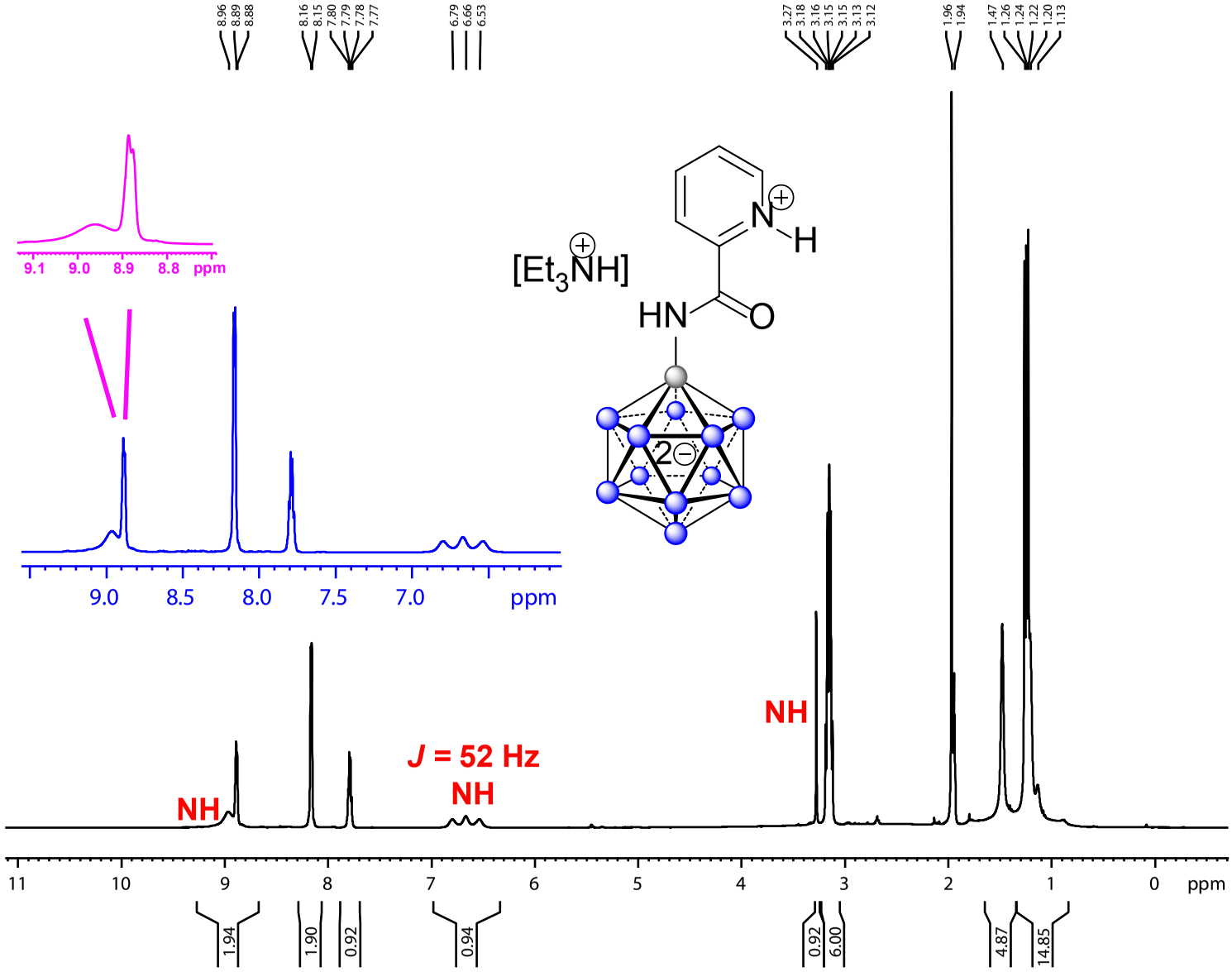
IV References

[1] V. Geis, K. Guttsche, C. Knapp, H. Scherer, R. Uzun, *Dalton Trans.* **2009**, 2687–2694.

[2] O. Bondarev, A. A. Khan, X. Tu, Y. V. Sevrugina, S. S. Jalisatgi, M. F. Hawthorne, *J. Am. Chem. Soc*. **2013**, *135*, 13204–13211.

[3] Y. Sun, J. Zhang, Y. Zhang, J. Liu, S. van der Veen, S. Duttwyler, *Chem. Eur. J.* **2018**, *24*, 10364–10371.

1H{11B} NMR 400MHz CD3CN

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PROCNO                 1

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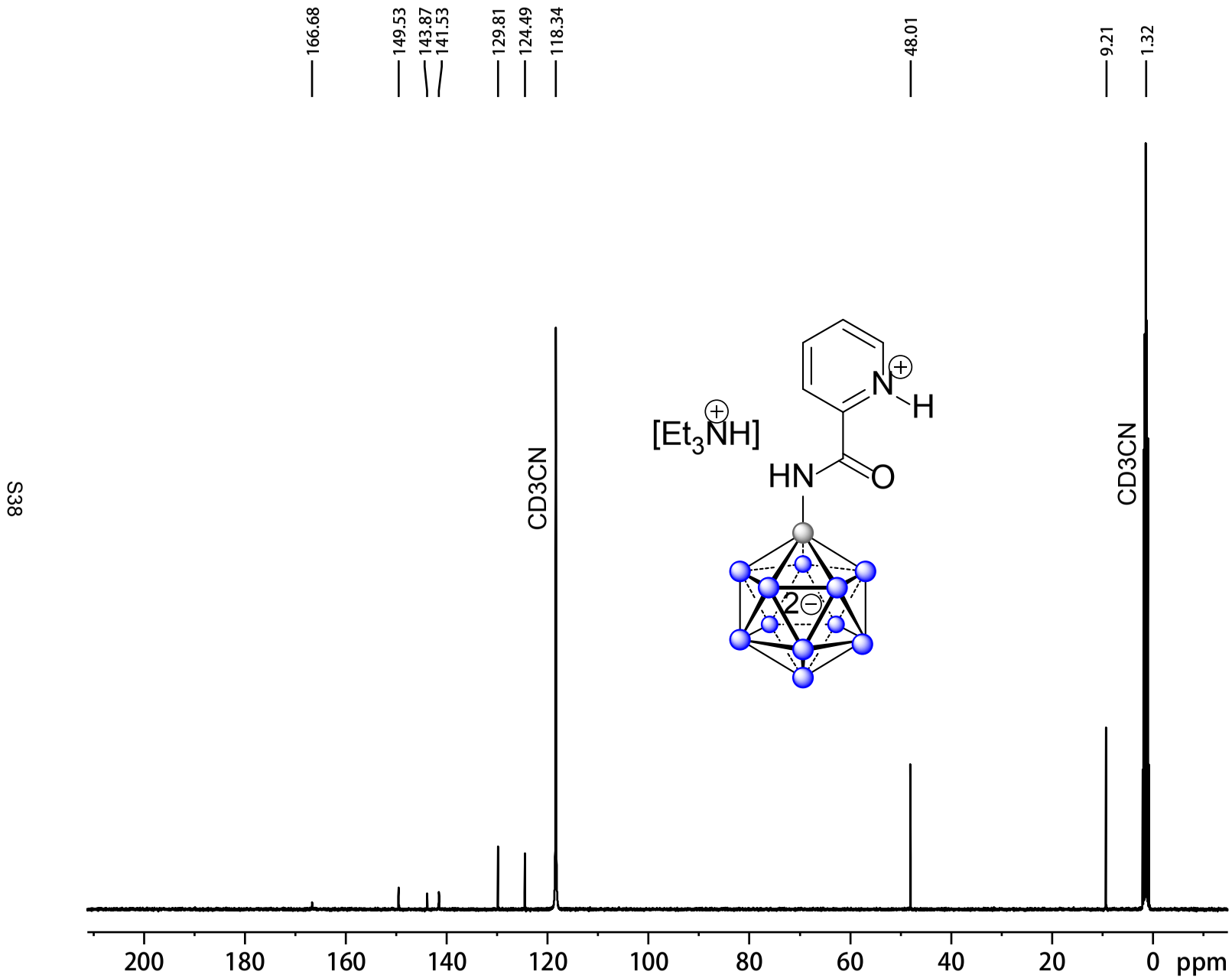
PULPROG         zgig30
TD               16384
SOLVENT          CD3CN
NS                  64
DS                   4
SWH            8012.820 Hz
FIDRES         0.489064 Hz
AQ             1.0223616 sec
RG                86.58
DW              62.400 usec
DE               6.50 usec
TE              294.0 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               15.00 usec
PLW1        12.50000000 W
SFO1        400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2          garp4
NUC2                11B
PCPD2            90.00 usec
PLW2        52.96599960 W
PLW12        0.64477998 W
SFO2        128.3776050 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300118 MHz
WDW                  EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

13C{1H} NMR 101MHz CD3CN

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Current Data Parameters
NAME      wt-01071_crst_09th_rt
EXPNO                  5
PROCNO                 1

F2 - Acquisition Parameters
Date_           20180517
Time              14.33
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                 2048
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               193.34
DW               16.800 usec
DE                6.50 usec
TE               294.9 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PLW1         53.00000000 W
SFO1        100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6126739 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
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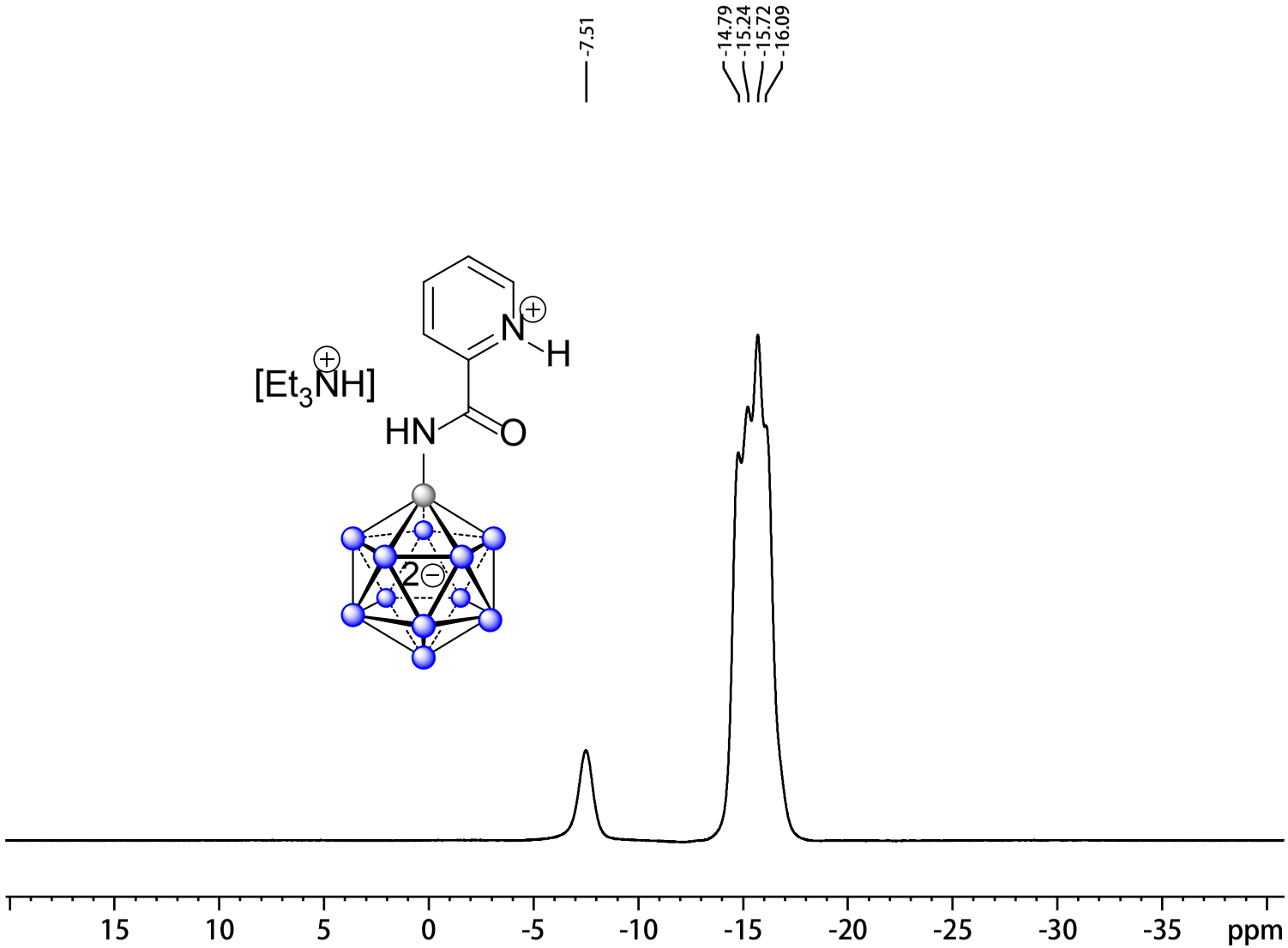
11B NMR 126 MHz CD3CN

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NAME      20180517_early_wt-01071_crst_9
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_          20171213
Time              20.40
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG             zg
TD                65536
SOLVENT           CD3CN
NS                  512
DS                    4
SWH           25510.203 Hz
FIDRES        0.389255 Hz
AQ            1.2845056 sec
RG                193.34
DW               19.600 usec
DE                6.50 usec
TE               293.5 K
D1            1.00000000 sec
TD0                   1

======== CHANNEL f1 =======
NUC1                 11B
P1                  9.93 usec
PLW1        52.96599960 W
SFO1        128.3776052 MHz

F2 - Processing parameters
SI                32768
SF          128.3776050 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```
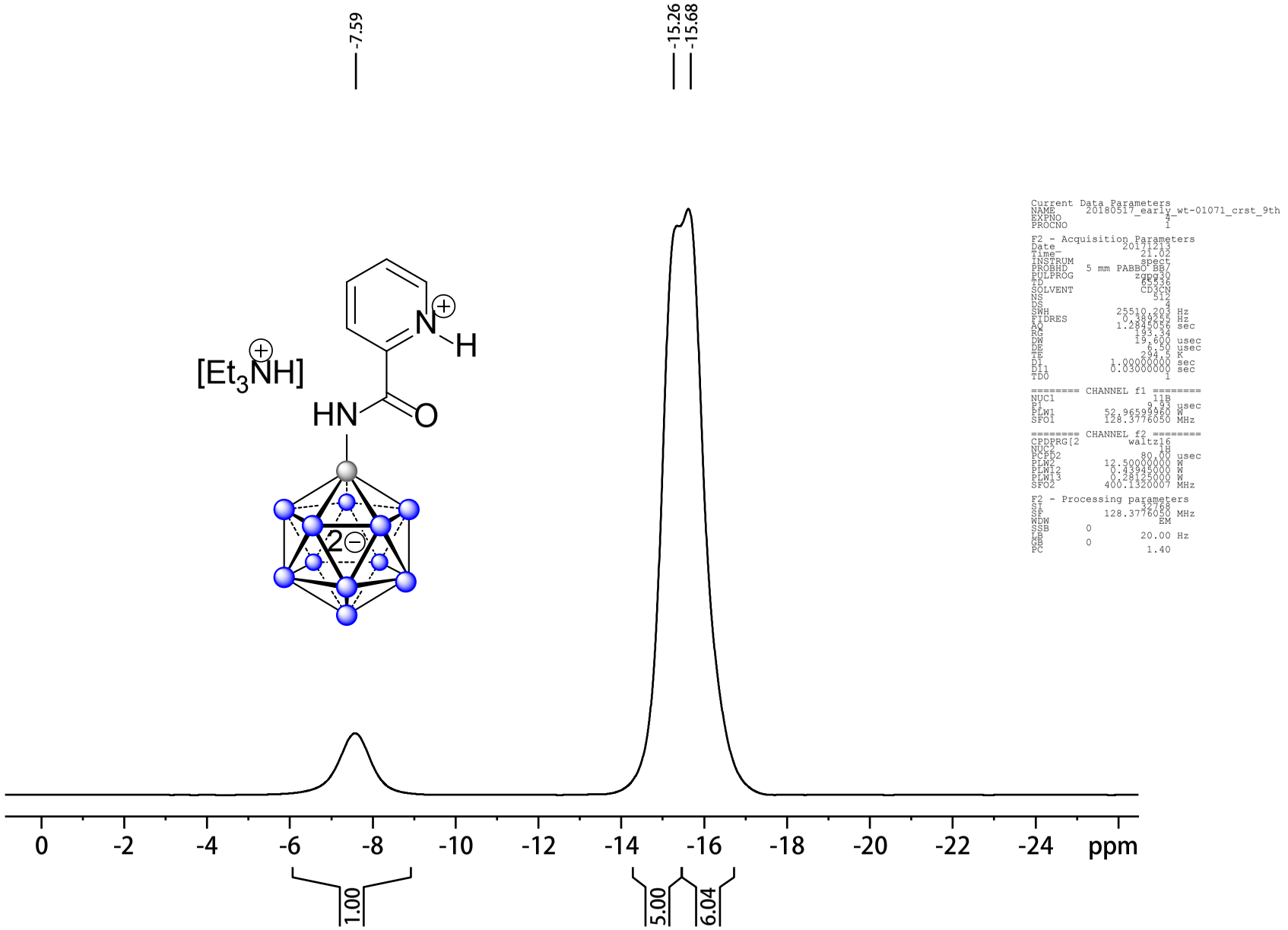

11B{1H} NMR 126 MHz CD3CN

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PROCNO                 1

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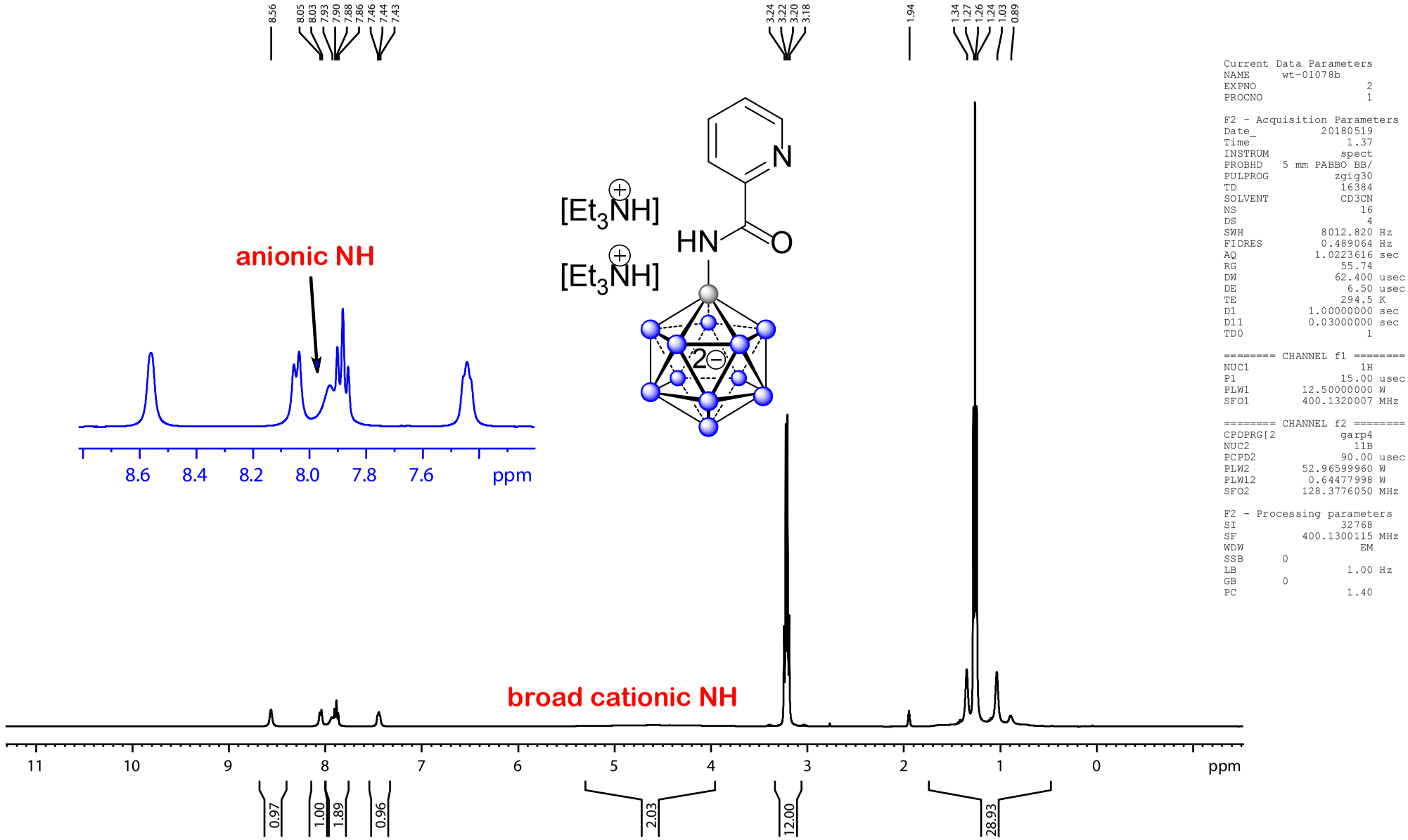
Time_              21.02
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                  512
DS                    4
SWH           25510.203 Hz
FIDRES        0.389255 Hz
AQ            1.2845056 sec
RG                193.34
DW               19.600 usec
DE                6.50 usec
TE                294.5 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 11B
P1                 9.93 usec
PLW1         52.96599960 W
SFO1        128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2        400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF          128.3776050 MHz
WDW                   EM
SSB                   0
LB                20.00 Hz
GB                    0
PC                 1.40
```

1H{11B} NMR 400MHz CD3CN

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Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20180519
Time               1.37
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgig30
TD              16384
SOLVENT          CD3CN
NS                  16
DS                   4
SWH           8012.820 Hz
FIDRES        0.489064 Hz
AQ           1.0223616 sec
RG              55.74
DW              62.400 usec
DE               6.50 usec
TE              294.5 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PLW1        12.50000000 W
SFO1        400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2          garp4
NUC2                11B
PCPD2             90.00 usec
PLW2        52.96599960 W
PLW12        0.64477998 W
SFO2        128.3776050 MHz

F2 - Processing parameters
SI                32768
SF          400.1300115 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```
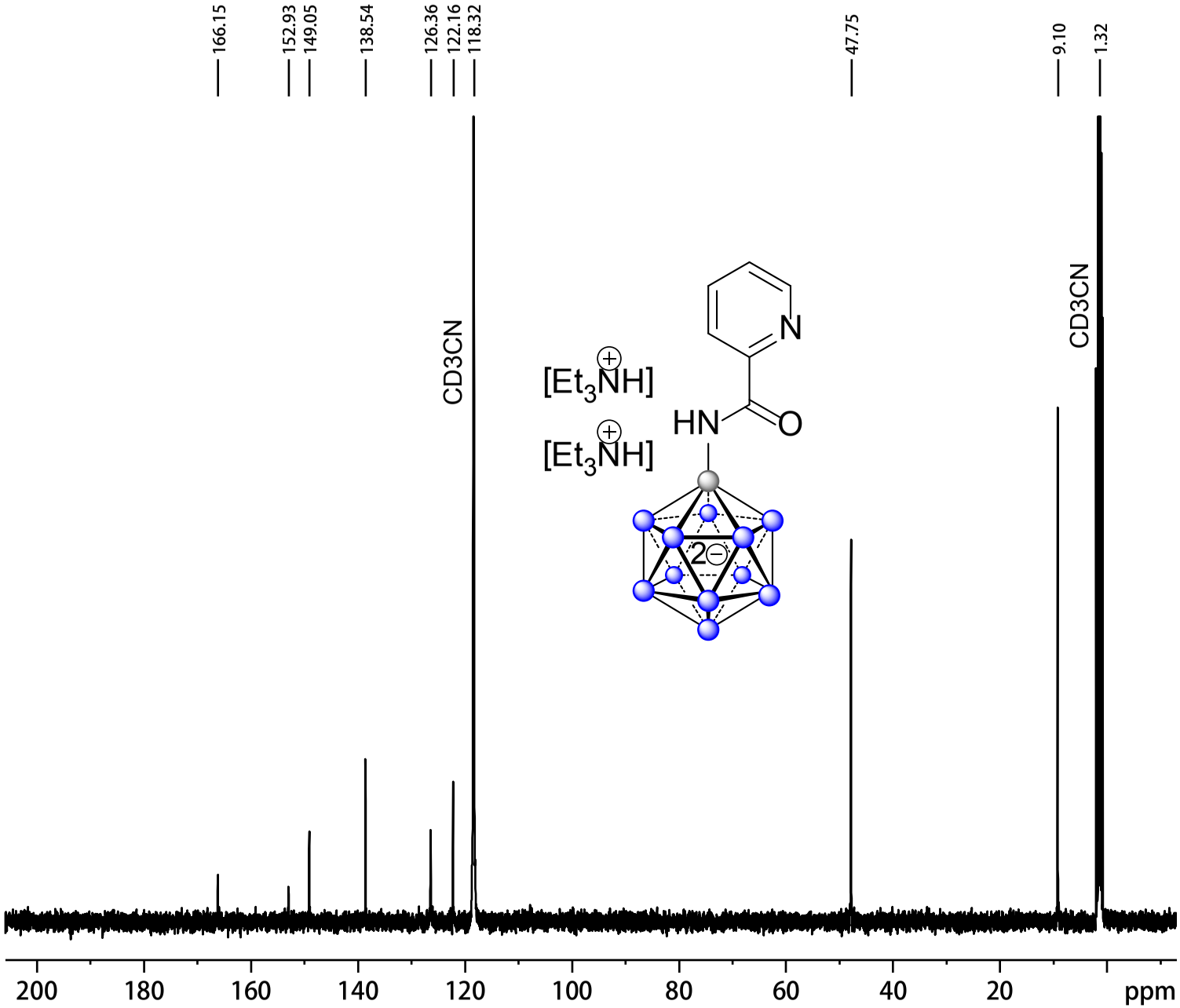

13C{1H} NMR 101MHz CD3CN

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Current Data Parameters
NAME      wt-01078b
EXPNO                 5
PROCNO                1

F2 - Acquisition Parameters
Date_          20180519
Time               2.13
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                 512
DS                   4
SWH          29761.904 Hz
FIDRES         0.454131 Hz
AQ             1.1010048 sec
RG                193.34
DW                16.800 usec
DE                 6.50 usec
TE                295.5 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1        53.00000000 W
SFO1       100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PLW2        12.50000000 W
PLW12        0.43945000 W
PLW13        0.28125000 W
SFO2       400.1316005 MHz

F2 - Processing parameters
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SF          100.6126762 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
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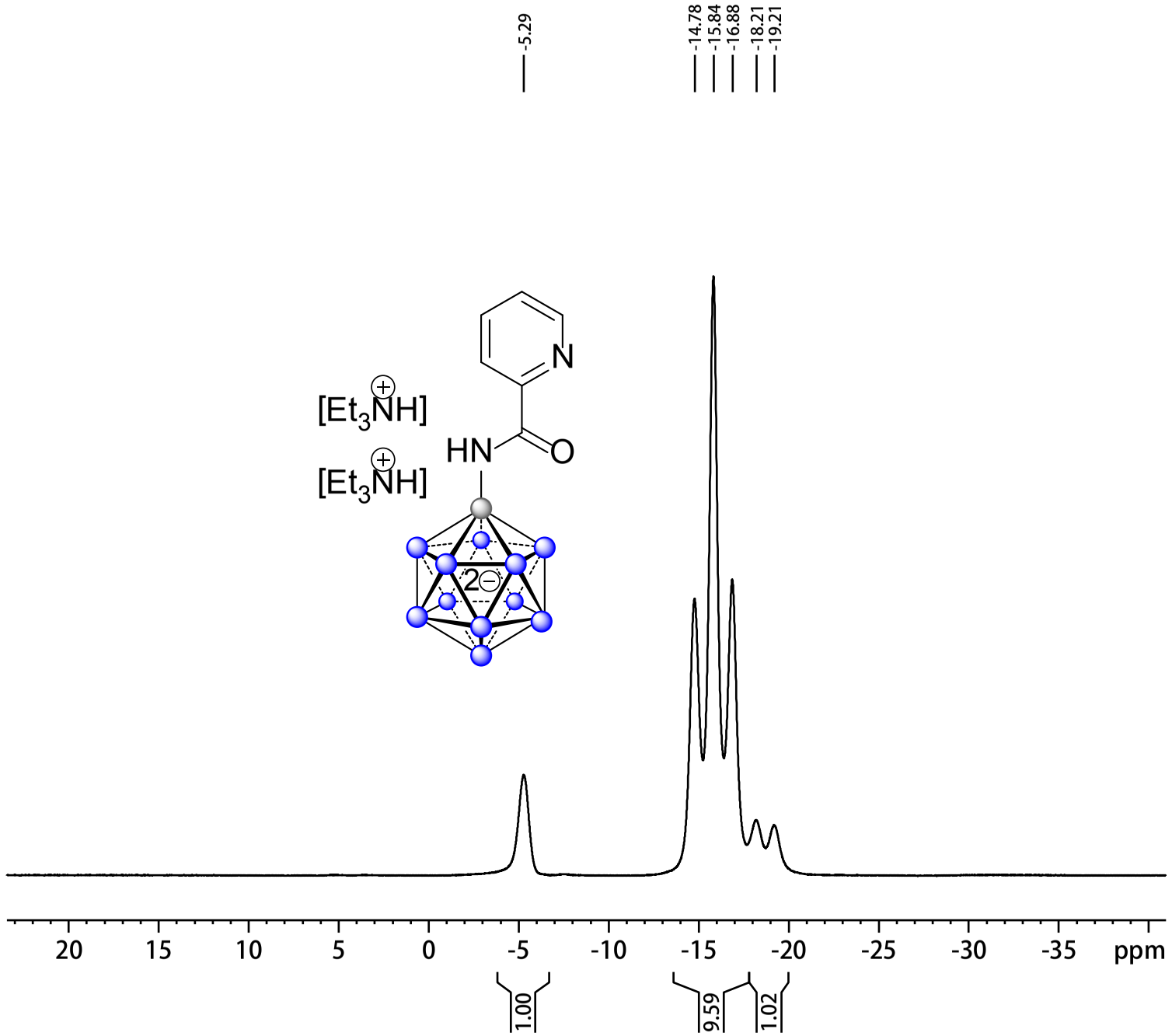


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EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
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Time                1.43
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 65536
SOLVENT            CD3CN
NS                   128
DS                     4
SWH            25510.203 Hz
FIDRES          0.389255 Hz
AQ             1.2845056 sec
RG                193.34
DW                19.600 usec
DE                 6.50 usec
TE                294.5 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  11B
P1                   9.93 usec
PLW1         52.96599960 W
SFO1         128.3776052 MHz

F2 - Processing parameters
SI                 32768
SF          128.3776050 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
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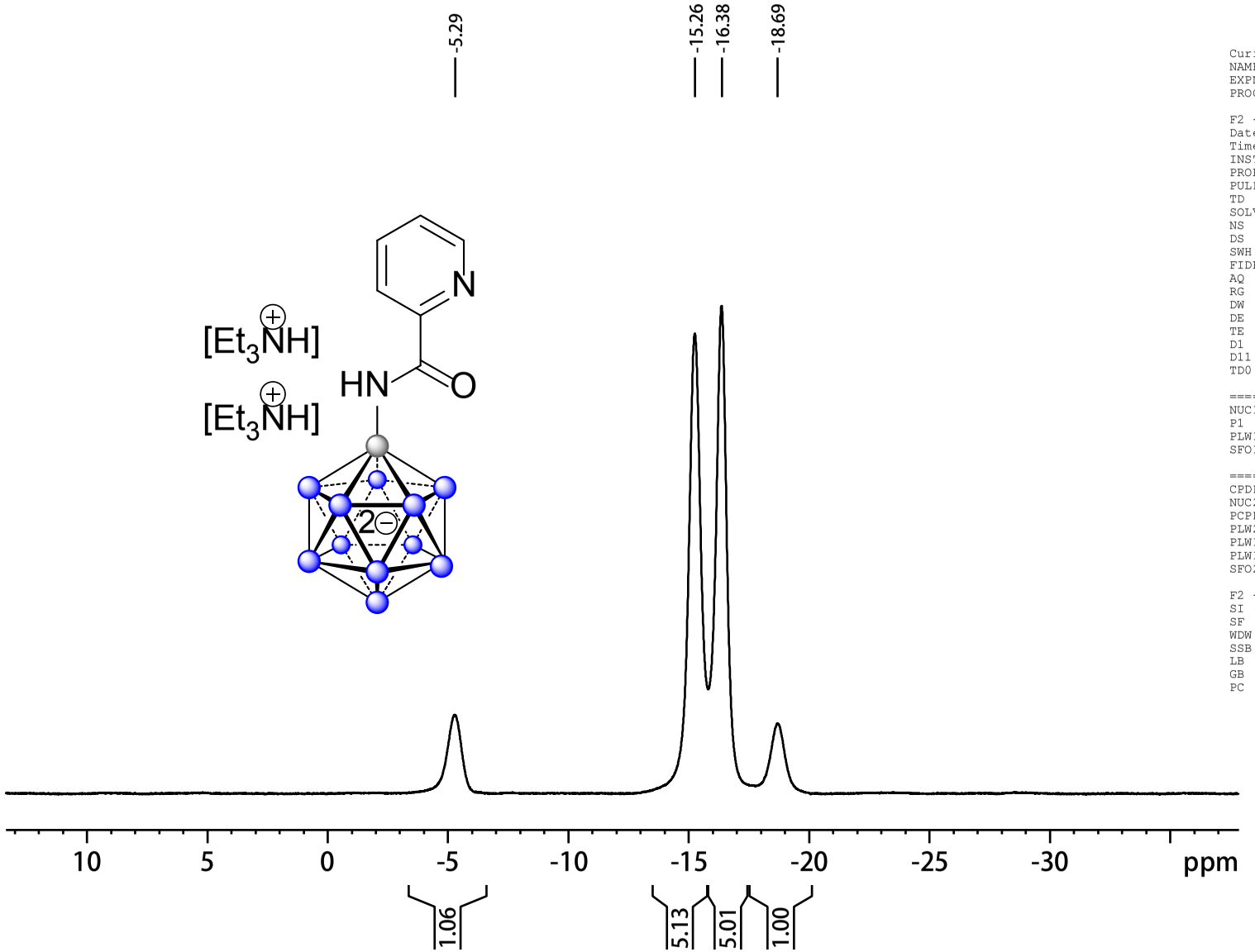


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Current Data Parameters
NAME      wt-01078b-[NEt3H]2[B12H11NHCOPy]
EXPNO                  4
PROCNO                 1

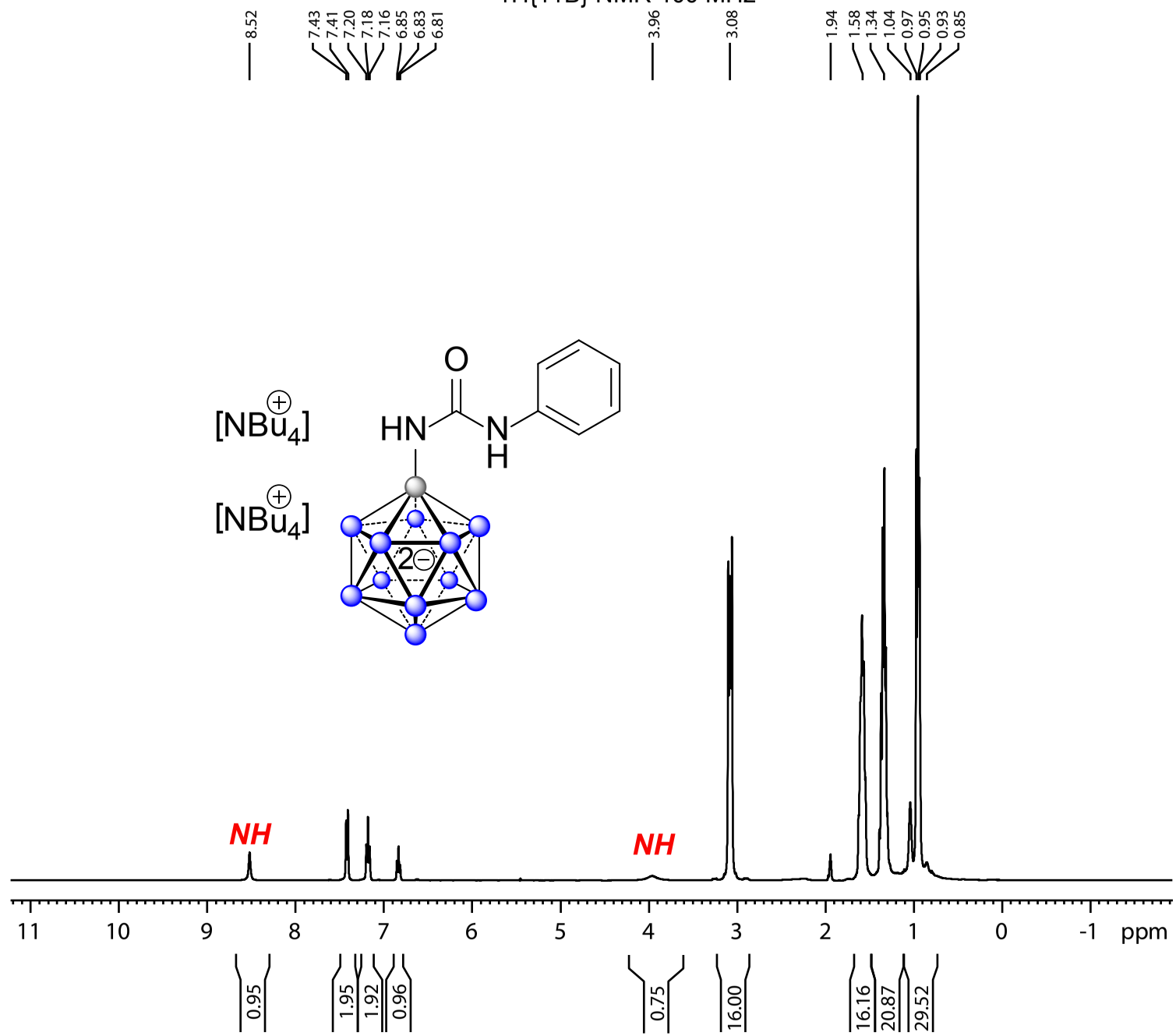
F2 - Acquisition Parameters
Date_           20180519
Time               1.49
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                  128
DS                    4
SWH           25510.203 Hz
FIDRES         0.389255 Hz
AQ            1.2845056 sec
RG               193.34
DW               19.600 usec
DE                6.50 usec
TE               295.1 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 11B
P1                  9.93 usec
PLW1         52.96599960 W
SFO1        128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2        400.1320007 MHz

F2 - Processing parameters
SI                 32768
SF          128.3776050 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20180602 [NBu4]2[B12H11NHCONHPh] 40mg dissolved in CD3CN
1H{11B} NMR 400 MHz

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Current Data Parameters
NAME      20180602-B12H11NHCONHPh
EXPNO                           2
PROCNO                          1

F2 - Acquisition Parameters
Date_              20180603
Time                   3.44
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG             zgig30
TD                   16384
SOLVENT              CD3CN
NS                      16
DS                       4
SWH                8012.820 Hz
FIDRES             0.489064 Hz
AQ                 1.0223616 sec
RG                     23.04
DW                    62.400 usec
DE                     6.50 usec
TE                    293.5 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PLW1          12.50000000 W
SFO1          400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2              garp4
NUC2                    11B
PCPD2                90.00 usec
PLW2          52.96599960 W
PLW12          0.64477998 W
SFO2          128.3776050 MHz

F2 - Processing parameters
SI                      32768
SF            400.1300118 MHz
WDW                        EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```
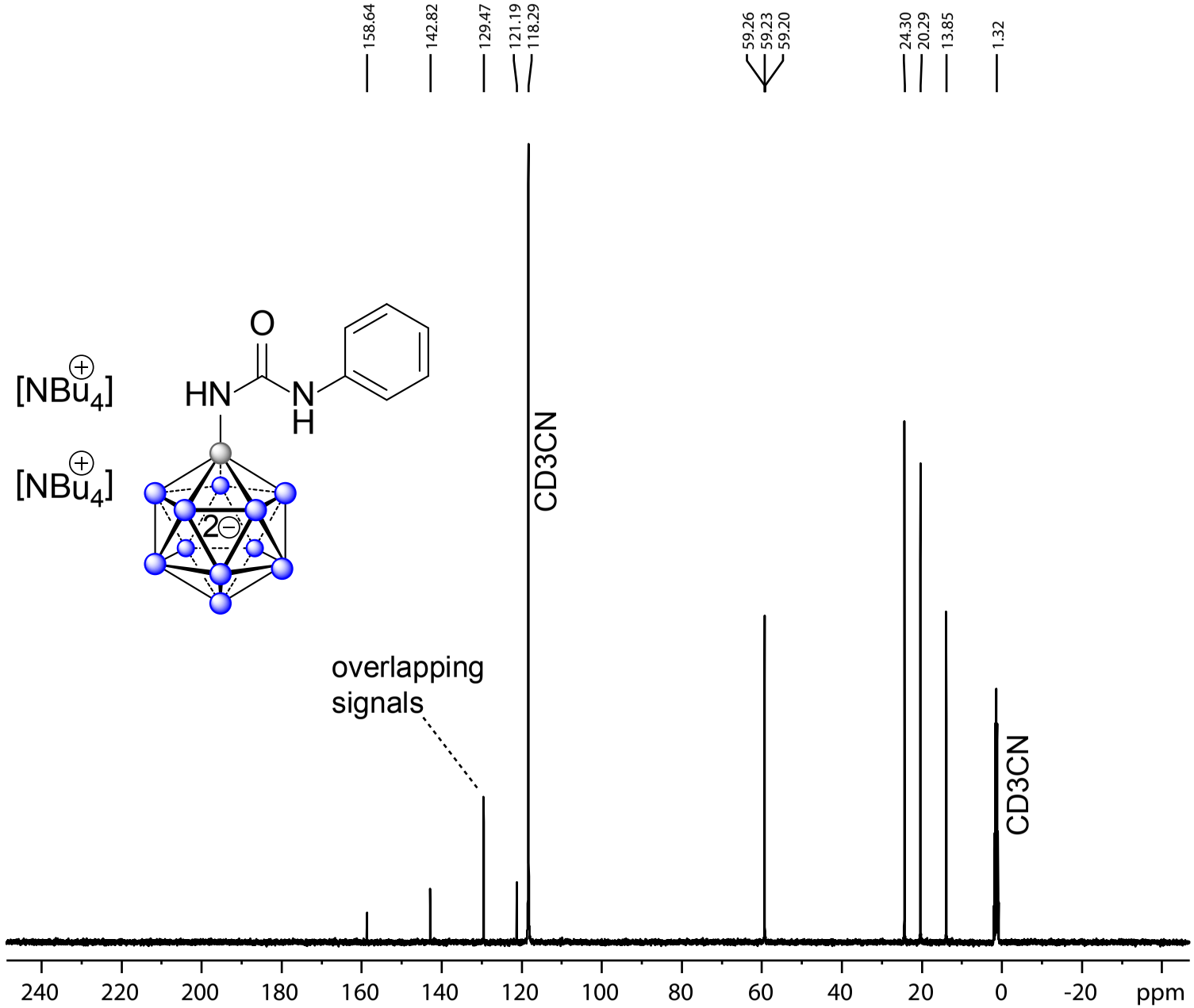

20180602 [NBu4]2[B12H11NHCONHPh] 40mg dissolved in CD3CN
13C{1H} NMR 101MHz

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Current Data Parameters
NAME      20180602-B12H11NHCONHPh
EXPNO                   5
PROCNO                  1

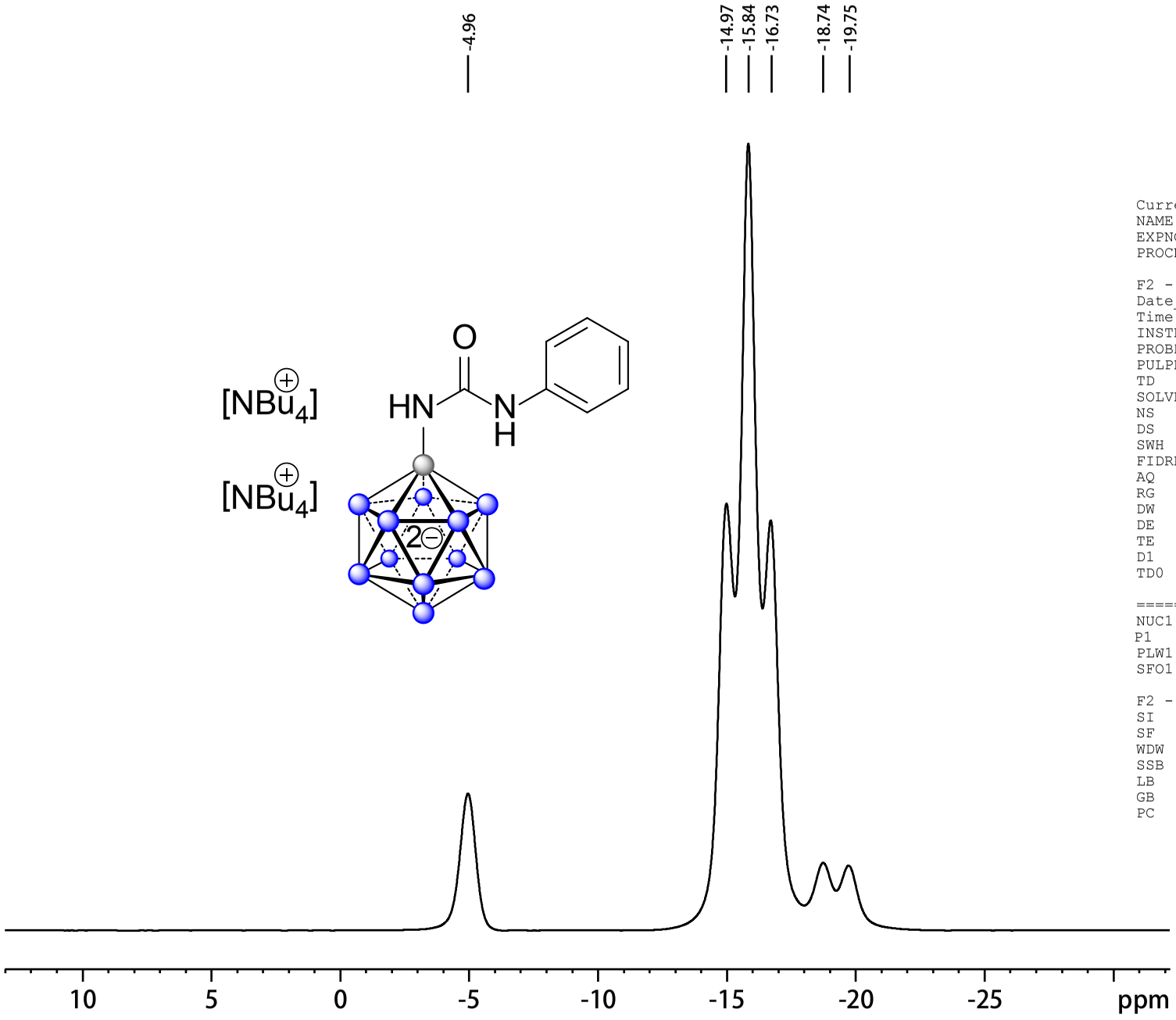
F2 - Acquisition Parameters
Date_           20180603
Time                4.20
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CD3CN
NS                   512
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                193.34
DW                16.800 usec
DE                 6.50 usec
TE                295.1 K
D1             1.50000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                 10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6126766 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20180602 [NBu4]2[B12H11NHCONHPh] 40mg dissolved in CD3CN
11B NMR 128 MHz

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EXPNO                           4
PROCNO                          1

F2 - Acquisition Parameters
Date_              20180603
Time                   3.56
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  65536
SOLVENT             CD3CN
NS                    128
DS                      4
SWH              25510.203 Hz
FIDRES            0.389255 Hz
AQ               1.2845056 sec
RG                  193.34
DW                  19.600 usec
DE                    6.50 usec
TE                   293.9 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   11B
P1                    9.93 usec
PLW1          52.96599960 W
SFO1          128.3776052 MHz

F2 - Processing parameters
SI                     32768
SF            128.3776050 MHz
WDW                     EM
SSB       0
LB                   20.00 Hz
GB        0
PC                    1.40
```
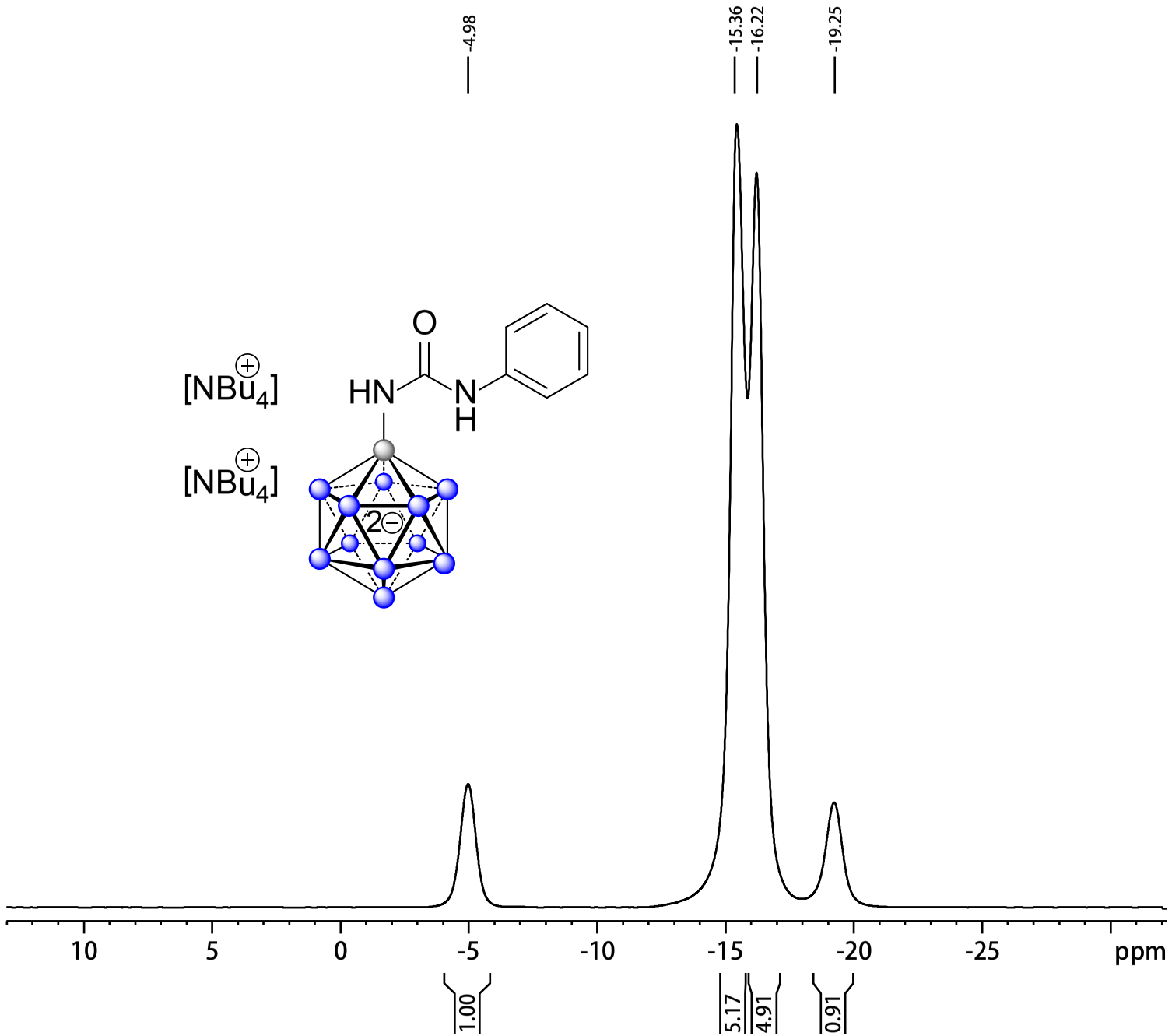

20180602 [NBu4]2[B12H11NHCONHPh] 40mg dissolved in CD3CN
11B{1H} NMR 128 MHz




```
Current Data Parameters
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EXPNO                           3
PROCNO                          1

F2 - Acquisition Parameters
Date_                    20180603
Time                         3.50
INSTRUM                     spect
PROBHD   5 mm PABBO BB/
PULPROG                    zgpg30
TD                          65536
SOLVENT                     CD3CN
NS                            128
DS                              4
SWH                     25510.203 Hz
FIDRES                   0.389255 Hz
AQ                       1.2845056 sec
RG                          193.34
DW                          19.600 usec
DE                           6.50 usec
TE                          294.3 K
D1                    1.00000000 sec
D11                   0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                          11B
P1                           9.93 usec
PLW1                52.96599960 W
SFO1                128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2                 waltz16
NUC2                          1H
PCPD2                       80.00 usec
PLW2                12.50000000 W
PLW12                0.43945000 W
PLW13                0.28125000 W
SFO2                400.1320007 MHz

F2 - Processing parameters
SI                            32768
SF                  128.3776050 MHz
WDW                             EM
SSB               0
LB                          20.00 Hz
GB                0
PC                           1.40
```
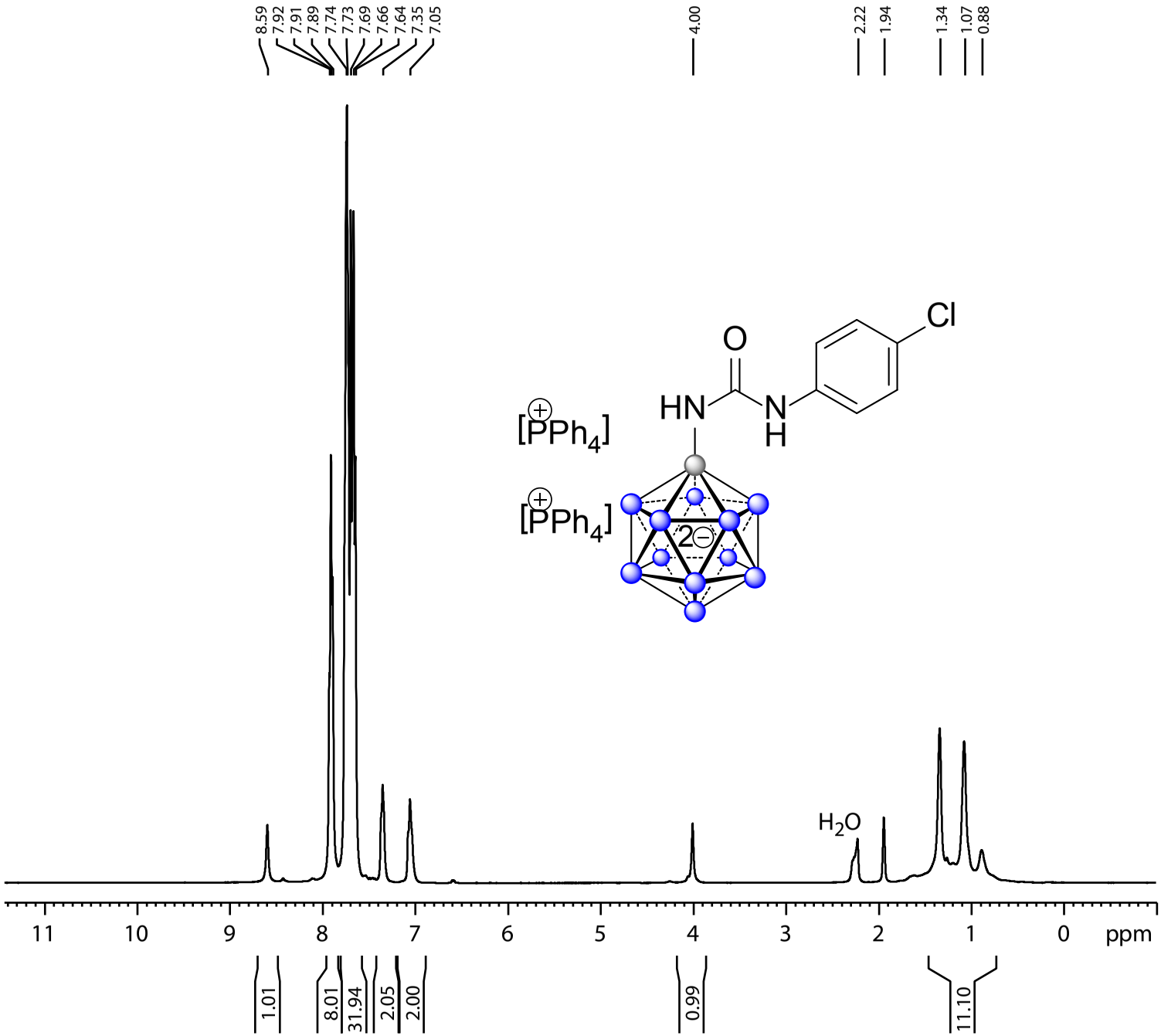
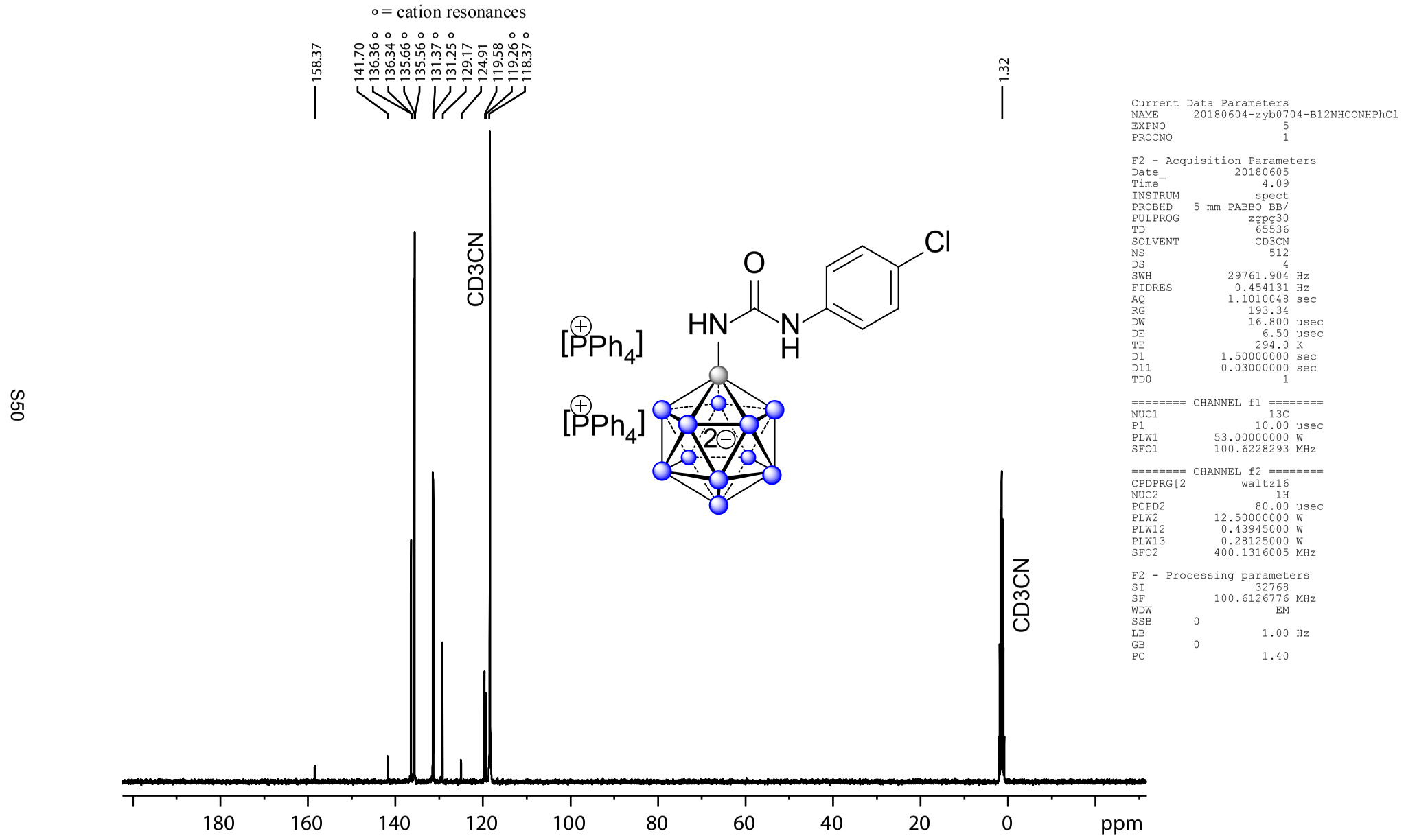

20180603 [PPh4]2[B12H11NHCONHPh] 50mg dissolved in CD3CN
1H{11B} NMR 400 MHz



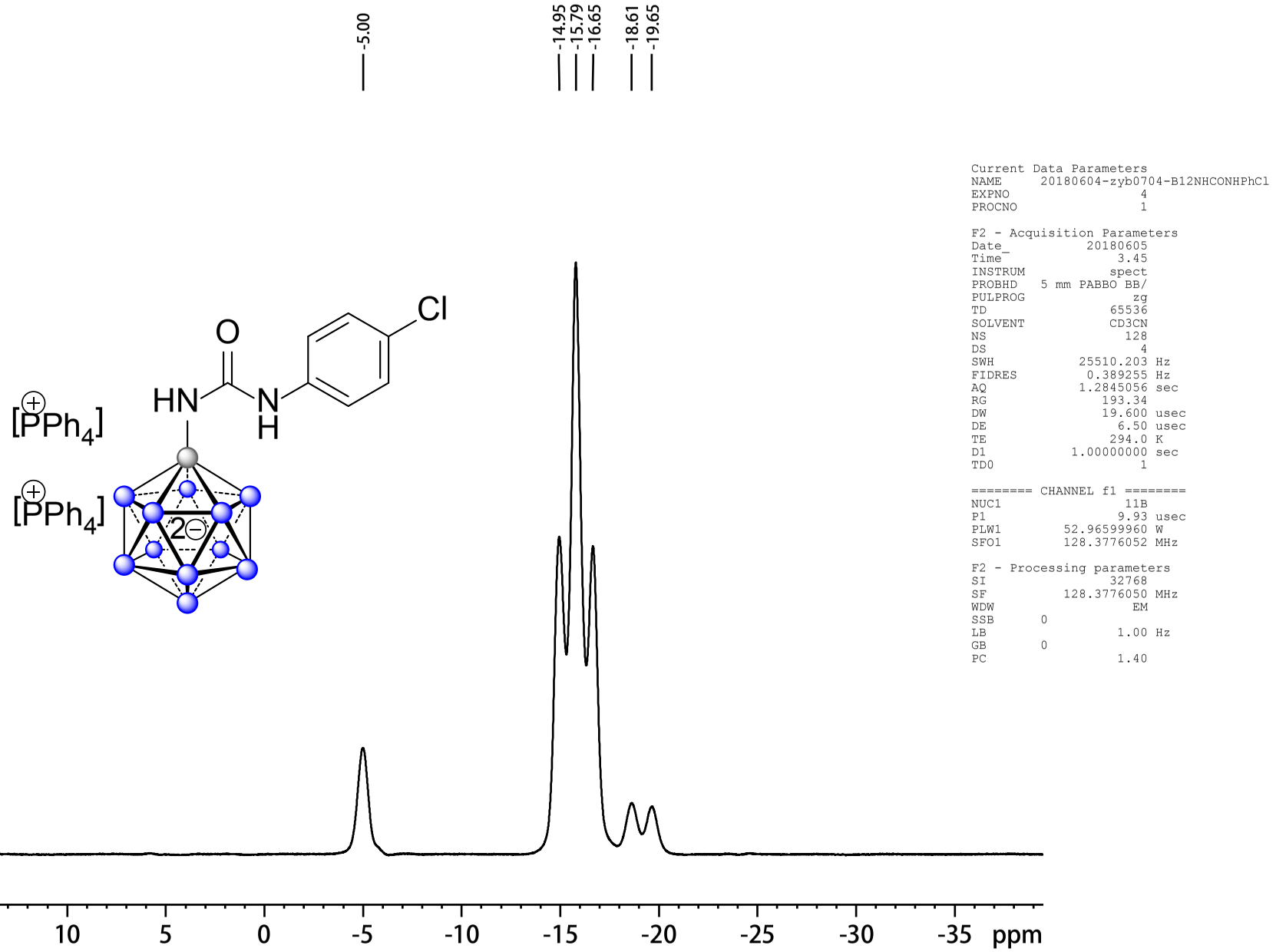

```
Current Data Parameters
NAME      20180604-zyb0704-B12NHCONHPhCl
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20180605
Time               3.33
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD              16384
SOLVENT          CD3CN
NS                  16
DS                   4
SWH           8012.820 Hz
FIDRES        0.489064 Hz
AQ           1.0223616 sec
RG              64.43
DW             62.400 usec
DE              6.50 usec
TE             294.4 K
D1          1.00000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1              15.00 usec
PLW1        12.50000000 W
SFO1       400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2           garp4
NUC2                11B
PCPD2           90.00 usec
PLW2        52.96599960 W
PLW12        0.64477998 W
SFO2       128.3776050 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300123 MHz
WDW                   EM
SSB       0
LB               1.00 Hz
GB        0
PC               1.40
```

20180603 [PPh4]2[B12H11NHCONHPh] 50mg dissolved in CD3CN
13C{1H} NMR 101MHz



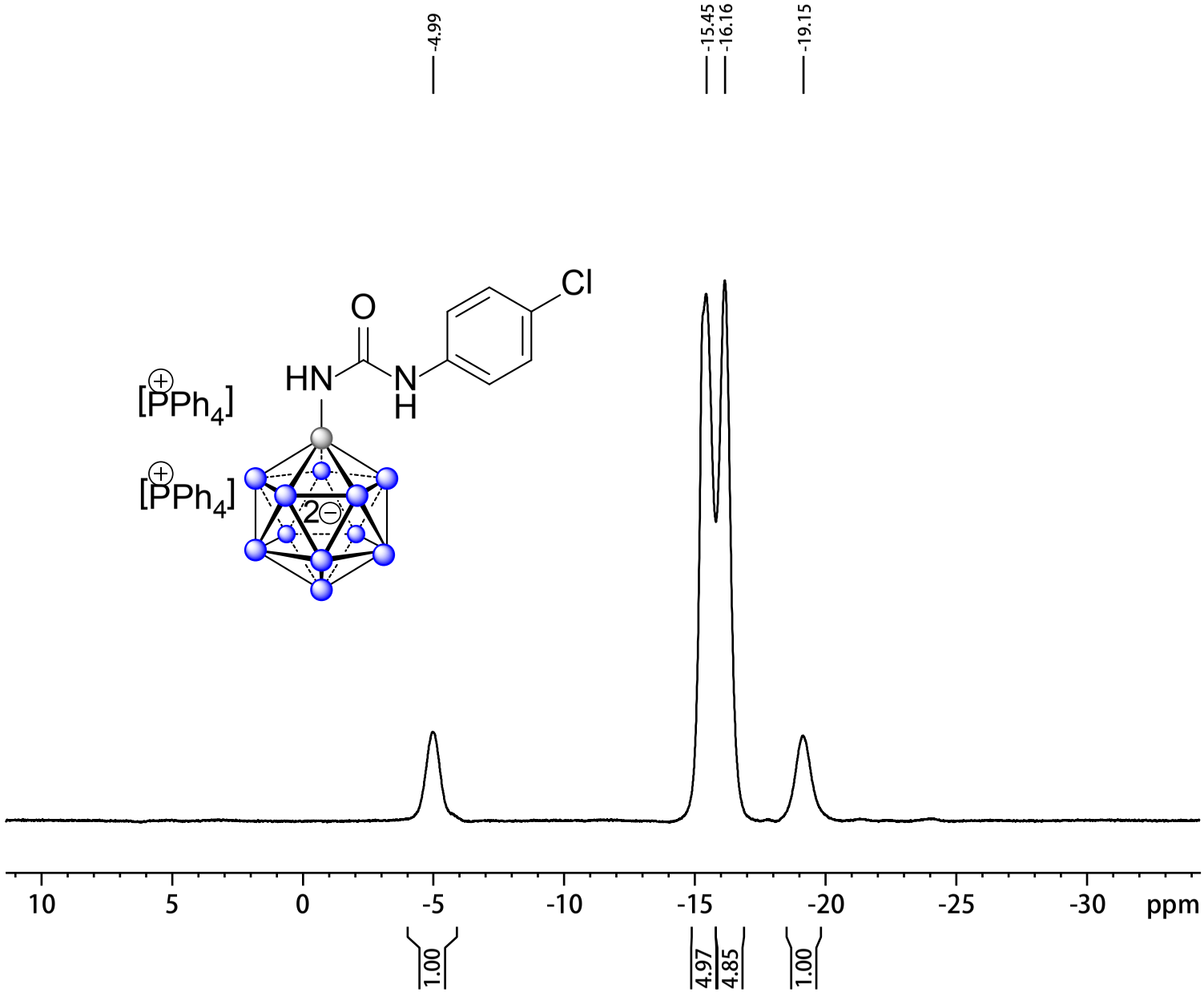

```
Current Data Parameters
NAME      20180604-zyb0704-B12NHCONHPhCl
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_           20180605
Time               4.09
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT            CD3CN
NS                   512
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                193.34
DW                16.800 usec
DE                 6.50 usec
TE                294.0 K
D1            1.50000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2              80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6126776 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20180603 [PPh4]2[B12H11NHCONHPh] 50mg dissolved in CD3CN
11B NMR 128 MHz



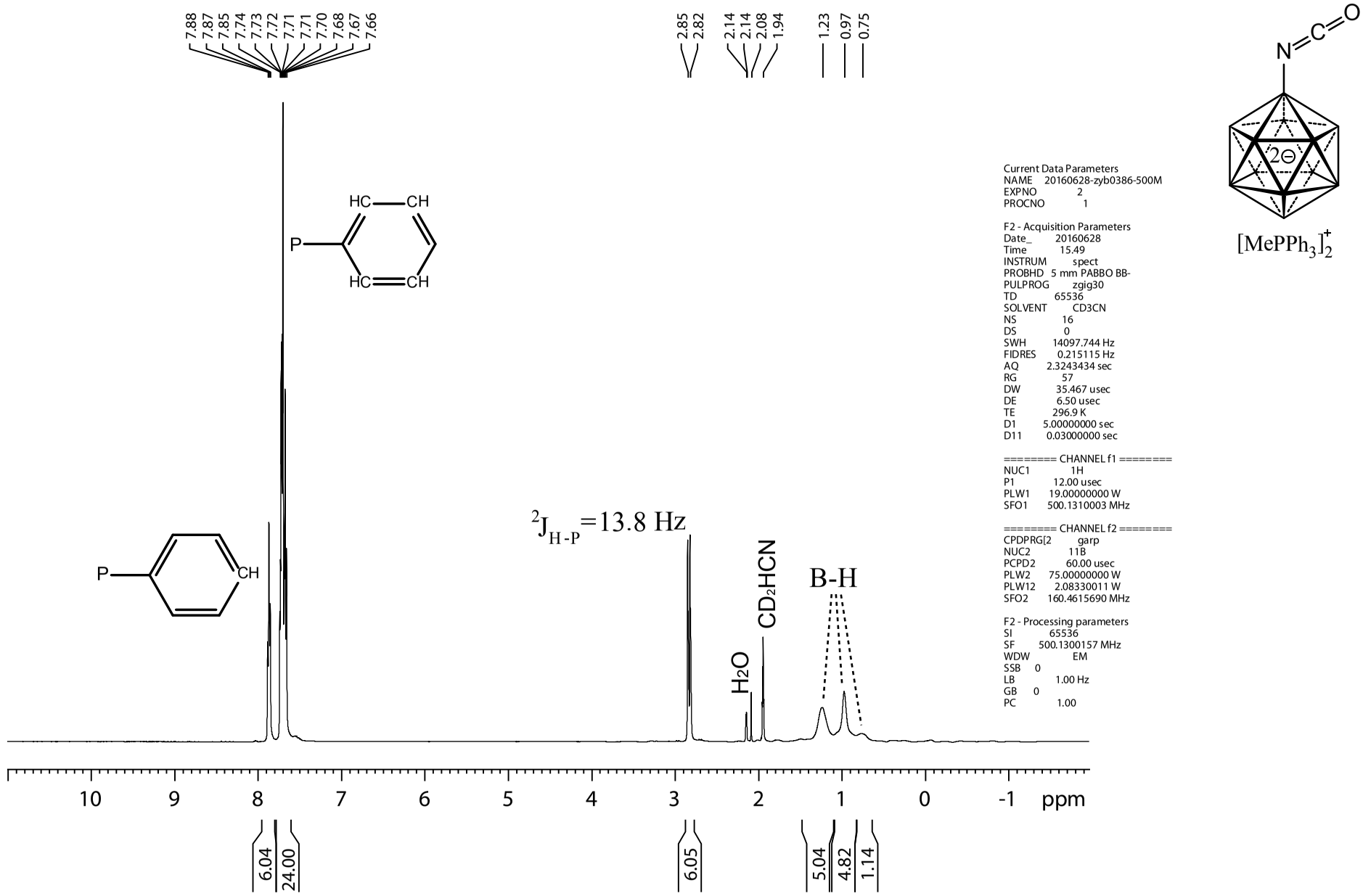

```
Current Data Parameters
NAME      20180604-zyb0704-B12NHCONHPhCl
EXPNO                 4
PROCNO                1

F2 - Acquisition Parameters
Date_          20180605
Time               3.45
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG             zg
TD                65536
SOLVENT           CD3CN
NS                  128
DS                    4
SWH           25510.203 Hz
FIDRES         0.389255 Hz
AQ            1.2845056 sec
RG               193.34
DW               19.600 usec
DE                6.50 usec
TE               294.0 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 11B
P1                  9.93 usec
PLW1        52.96599960 W
SFO1       128.3776052 MHz

F2 - Processing parameters
SI                32768
SF          128.3776050 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

20180603 [PPh4]2[B12H11NHCONHPh] 50mg dissolved in CD3CN
11B{1H} NMR 128 MHz




```
Current Data Parameters
NAME      20180604-zyb0704-B12NHCONHPhCl
EXPNO                 3
PROCNO                1

F2 - Acquisition Parameters
Date_           20180605
Time              3.39
INSTRUM          spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CD3CN
NS                 128
DS                   4
SWH          25510.203 Hz
FIDRES        0.389255 Hz
AQ           1.2845056 sec
RG              193.34
DW              19.600 usec
DE               6.50 usec
TE              294.1 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               11B
P1                9.93 usec
PLW1        52.96599960 W
SFO1       128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2        waltz16
NUC2               1H
PCPD2            80.00 usec
PLW2        12.50000000 W
PLW12        0.43945000 W
PLW13        0.28125000 W
SFO2       400.1320007 MHz

F2 - Processing parameters
SI                32768
SF         128.3776050 MHz
WDW                EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

20160629 20 mg [MePPh3]2[B12H11NCO] dissolved in 0.6 mL CD3CN , 1H{11B} NMR, 500MHz



Current Data Parameters
NAME 20160628-zyb0386-500M
EXPNO 2
PROCNO 1

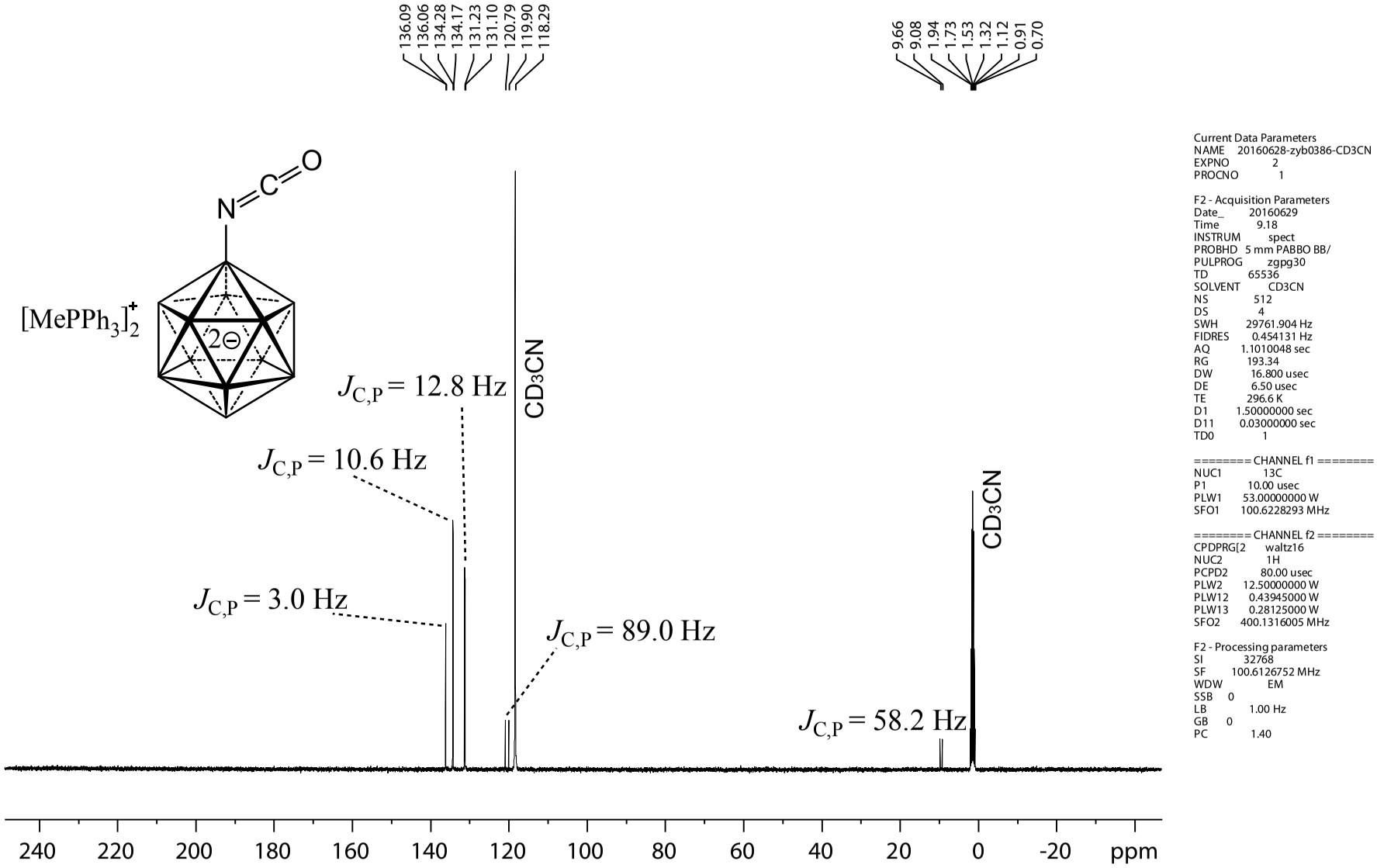
F2 - Acquisition Parameters
Date_ 20160628
Time 15.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgig30
TD 65536
SOLVENT CD3CN
NS 16
DS 0
SWH 14097.744 Hz
FIDRES 0.215115 Hz
AQ 2.3243434 sec
RG 57
DW 35.467 usec
DE 6.50 usec
TE 296.9 K
D1 5.00000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 12.00 usec
PLW1 19.00000000 W
SFO1 500.1310003 MHz

======== CHANNEL f2 ========
CPDPRG[2 garp
NUC2 11B
PCPD2 60.00 usec
PLW2 75.00000000 W
PLW12 2.08330011 W
SFO2 160.4615690 MHz

F2 - Processing parameters
SI 65536
SF 500.1300157 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00

20160629 20 mg [MePPh3]2[B12H11NCO] dissolved in 0.6 mL CD3CN, 1H NMR, 400MHz
signal of NCO not detected



Current Data Parameters
NAME 20160628-zyb0386-CD3CN
EXPNO 2
PROCNO 1

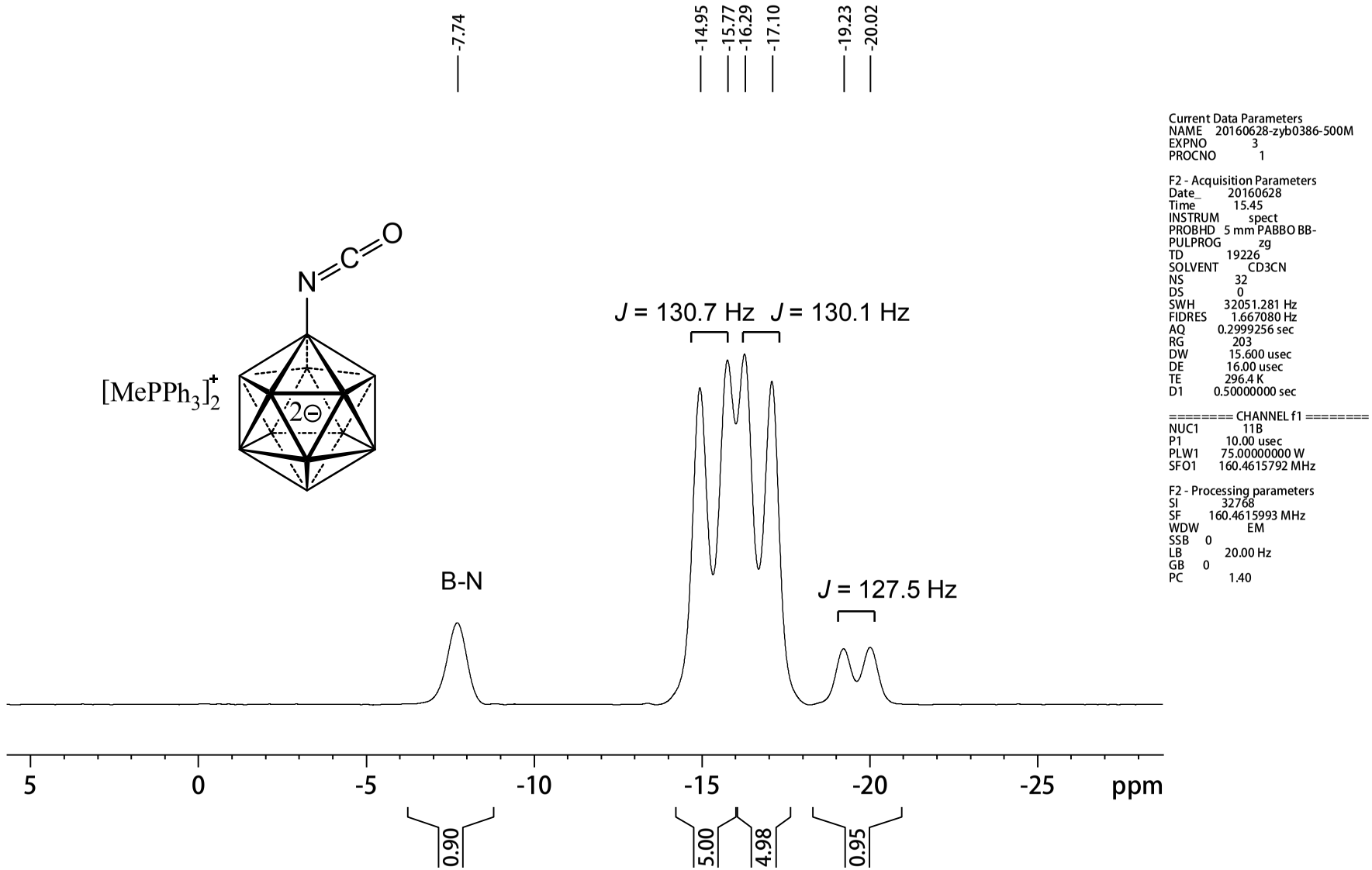
F2 - Acquisition Parameters
Date_ 20160629
Time 9.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CD3CN
NS 512
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 193.34
DW 16.800 usec
DE 6.50 usec
TE 296.6 K
D1 1.50000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.00 usec
PLW1 53.00000000 W
SFO1 100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 12.50000000 W
PLW12 0.43945000 W
PLW13 0.28125000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126752 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

20 mg [MePPh3]2[B12H11NCO] dissolved in 0.6 mL CD3CN
11B NMR,160MHz



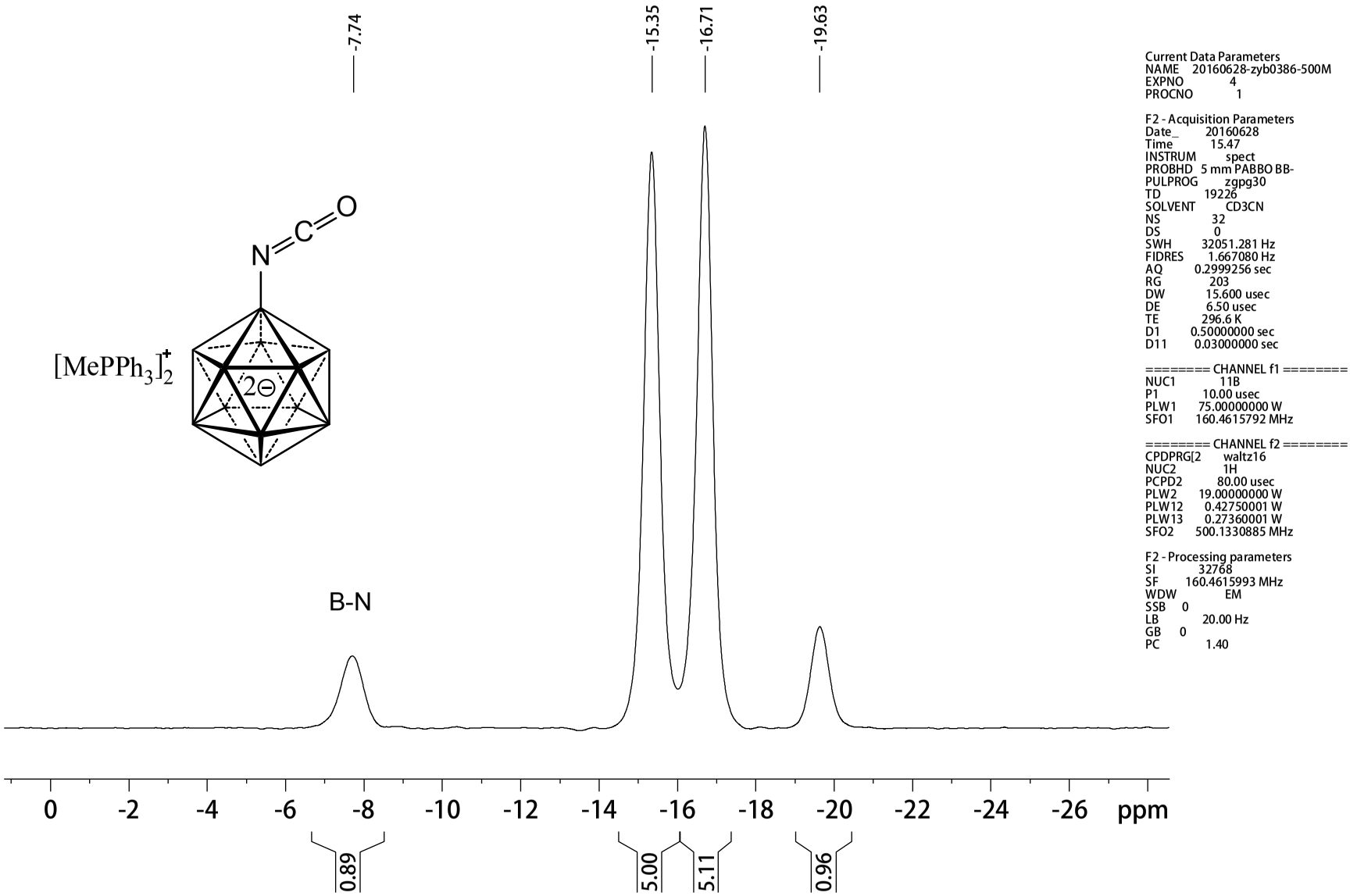
Current Data Parameters
NAME 20160628-zyb0386-500M
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20160628
Time 15.45
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 19226
SOLVENT CD3CN
NS 32
DS 0
SWH 32051.281 Hz
FIDRES 1.667080 Hz
AQ 0.2999256 sec
RG 203
DW 15.600 usec
DE 16.00 usec
TE 296.4 K
D1 0.50000000 sec

======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

F2 - Processing parameters
SI 32768
SF 160.4615993 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40

20 mg [MePPh3]2[B12H11NCO] dissolved in 0.6 mL CD3CN
11B{1H} NMR,160MHz



Current Data Parameters
NAME 20160628-zyb0386-500M
EXPNO 4
PROCNO 1

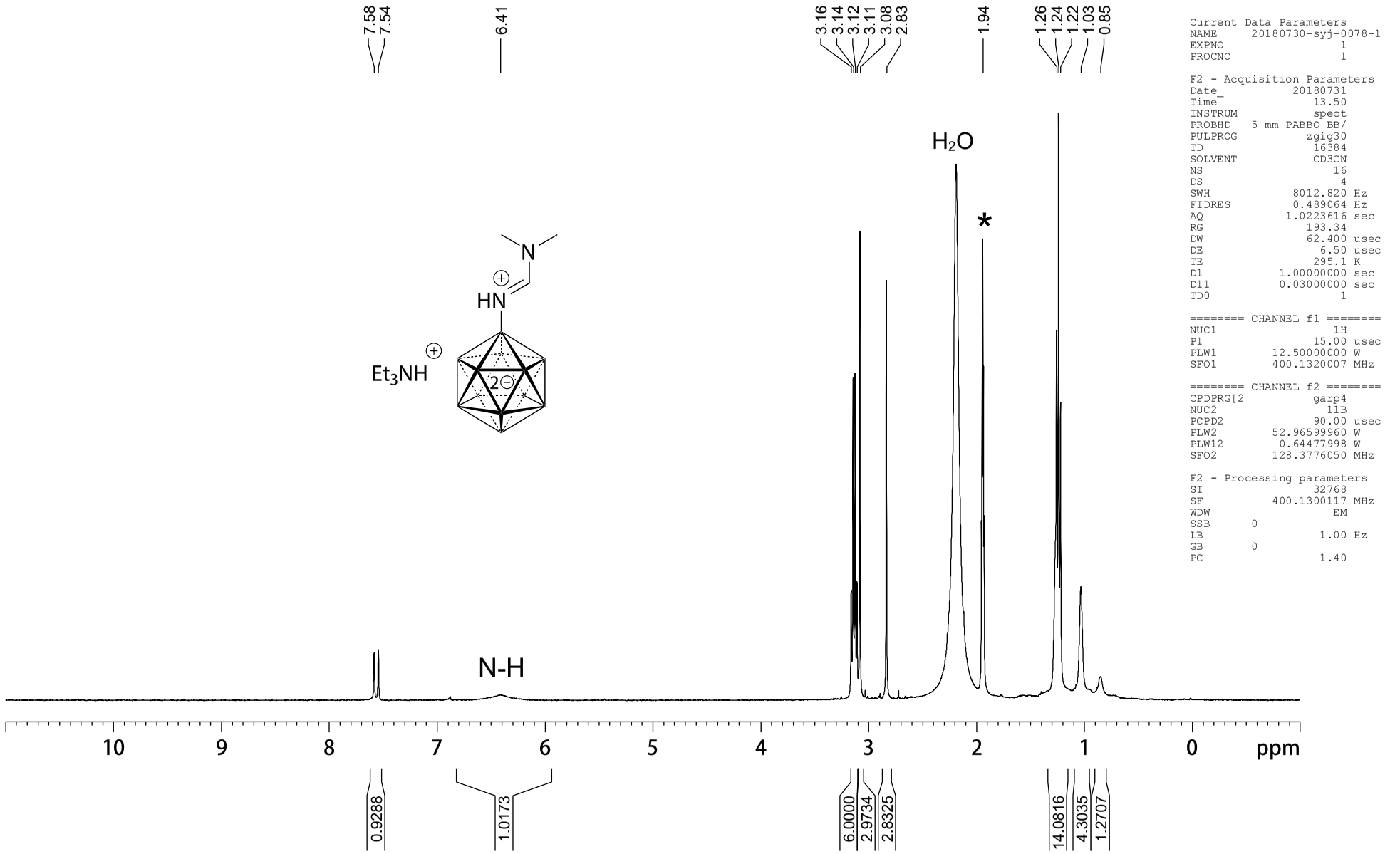
F2 - Acquisition Parameters
Date_ 20160628
Time 15.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 19226
SOLVENT CD3CN
NS 32
DS 0
SWH 32051.281 Hz
FIDRES 1.667080 Hz
AQ 0.2999256 sec
RG 203
DW 15.600 usec
DE 6.50 usec
TE 296.6 K
D1 0.50000000 sec
D11 0.03000000 sec

======== CHANNEL f1 ========
NUC1 11B
P1 10.00 usec
PLW1 75.00000000 W
SFO1 160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PLW2 19.00000000 W
PLW12 0.42750001 W
PLW13 0.27360001 W
SFO2 500.1330885 MHz

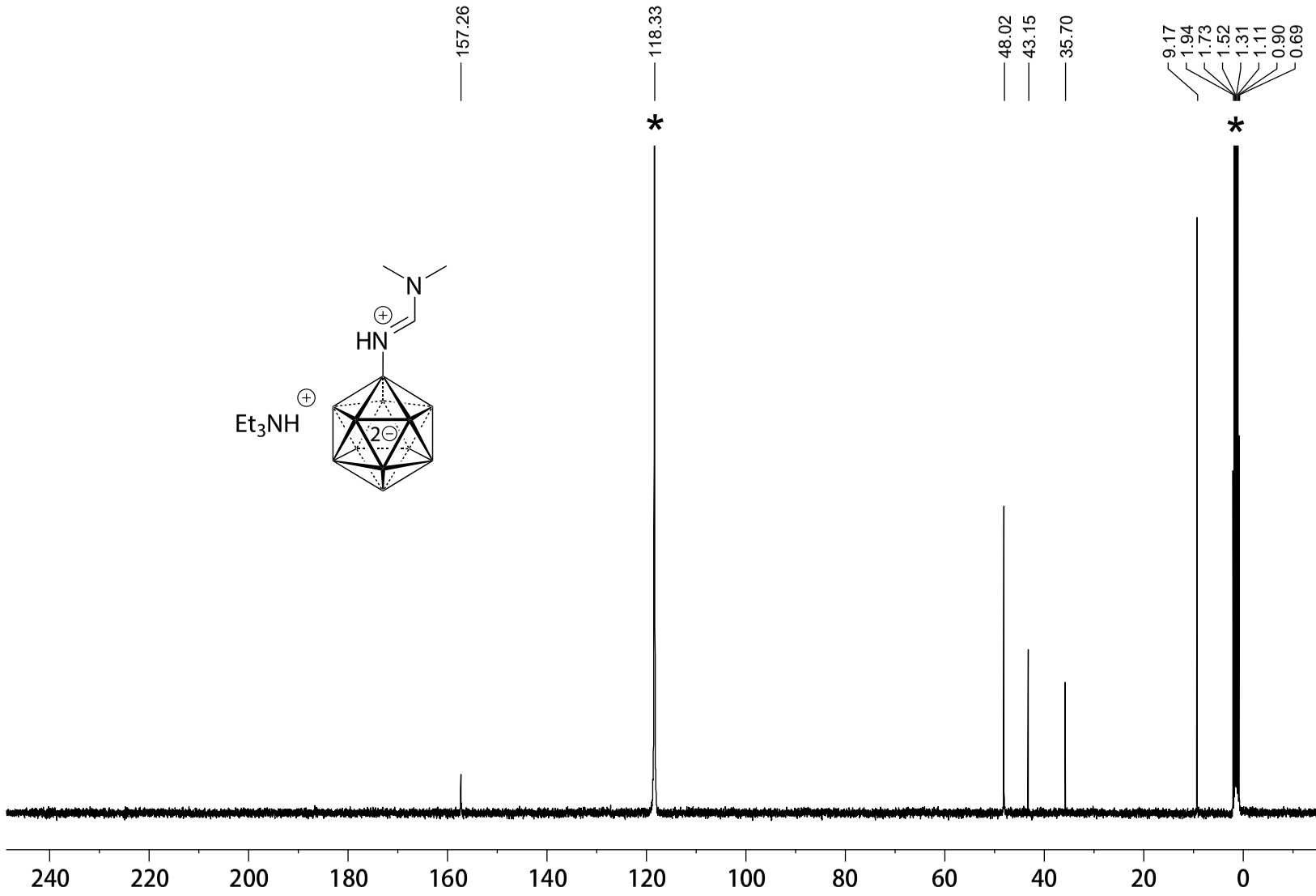
F2 - Processing parameters
SI 32768
SF 160.4615993 MHz
WDW EM
SSB 0
LB 20.00 Hz
GB 0
PC 1.40

20150313-syj-0077-2, Et3NHB12H11NHCHNMe2
20150313, 400 MHz, 1H{11B}, 12.4mg in 0.6ml CD3CN*



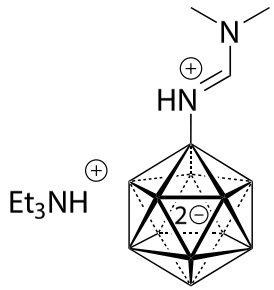

```
Current Data Parameters
NAME      20180730-syj-0078-1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20180731
Time               13.50
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgig30
TD                16384
SOLVENT           CD3CN
NS                   16
DS                    4
SWH             8012.820 Hz
FIDRES             0.489064 Hz
AQ              1.0223616 sec
RG                193.34
DW                 62.400 usec
DE                  6.50 usec
TE                295.1 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PLW1          12.50000000 W
SFO1          400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2             garp4
NUC2                 11B
PCPD2              90.00 usec
PLW2          52.96599960 W
PLW12          0.64477998 W
SFO2          128.3776050 MHz

F2 - Processing parameters
SI                 32768
SF            400.1300117 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20150313-syj-0077-2, Et3NHB12H11NHCHNMe2
20150313, 100 MHz, 13{1H}, 12.4mg in 0.6ml CD3CN*



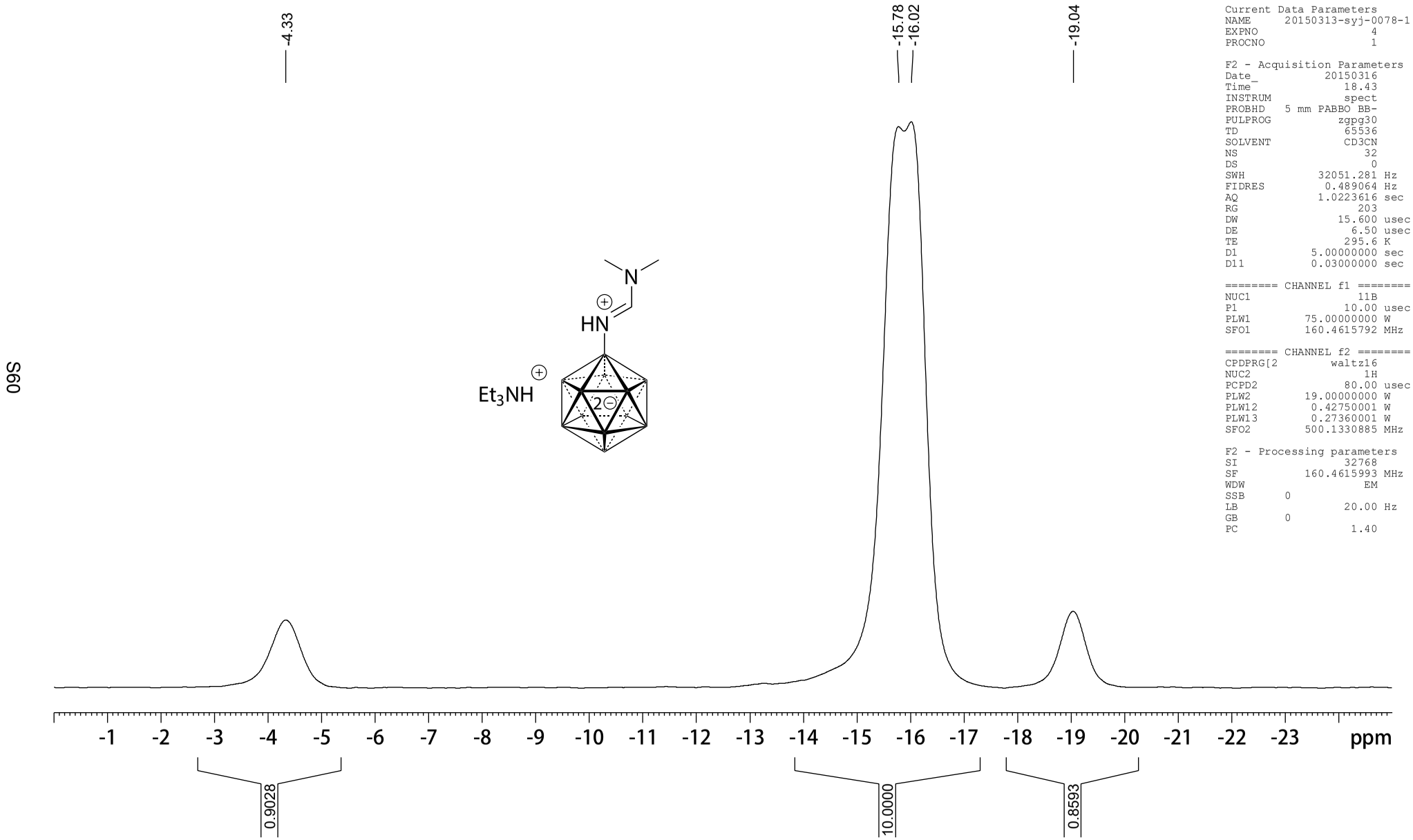

```
Current Data Parameters
NAME      20150313-syj-0078-1
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_            20150314
Time                12.51
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CD3CN
NS                  1024
DS                     4
SWH            29761.904 Hz
FIDRES          0.454131 Hz
AQ             1.1010048 sec
RG                193.34
DW                16.800 usec
DE                 6.50 usec
TE        0 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                  1H
PCPD2               80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6126766 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20150313-syj-0077-2, Et3NHB12H11NHCHNMe2
20150316, 160 MHz, 11B, 12.4mg in 0.6ml CD3CN



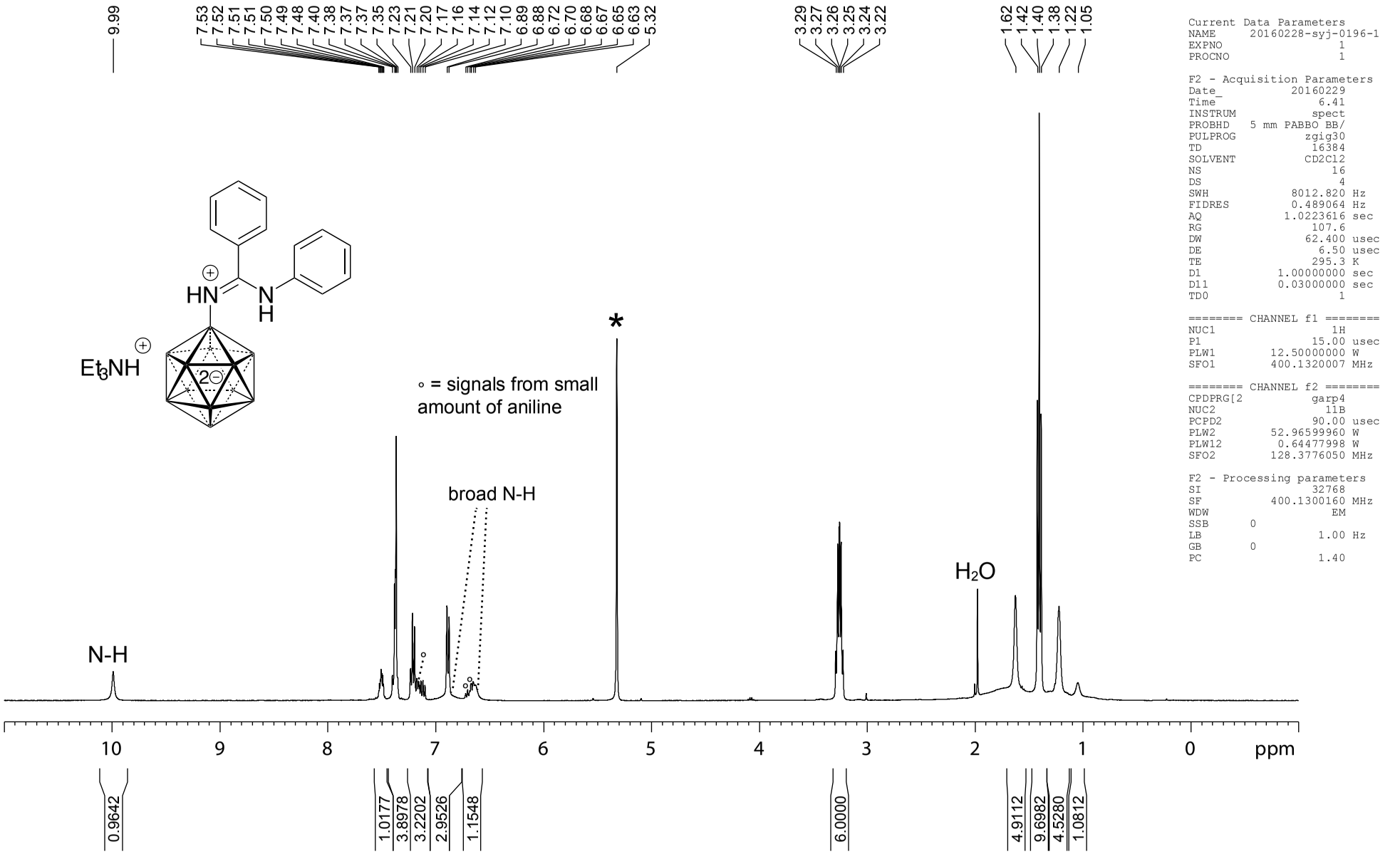

```
Current Data Parameters
NAME      20150313-syj-0078-1
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150316
Time                  18.38
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CD3CN
NS                       16
DS                        2
SWH               32051.281 Hz
FIDRES             0.489064 Hz
AQ                1.0223616 sec
RG                      203
DW                   15.600 usec
DE                    6.50 usec
TE                   293.6 K
D1             2.00000000 sec

======== CHANNEL f1 ========
NUC1                    11B
P1                    10.00 usec
PLW1          75.00000000 W
SFO1          160.4615792 MHz

F2 - Processing parameters
SI                      32768
SF            160.4615790 MHz
WDW                        EM
SSB       0
LB                    10.00 Hz
GB        0
PC                     1.40
```

20150313-syj-0077-2, Et3NHB12H11NHCHNMe2
20150316, 160 MHz, 11B{1H}, 12.4mg in 0.6ml CD3CN



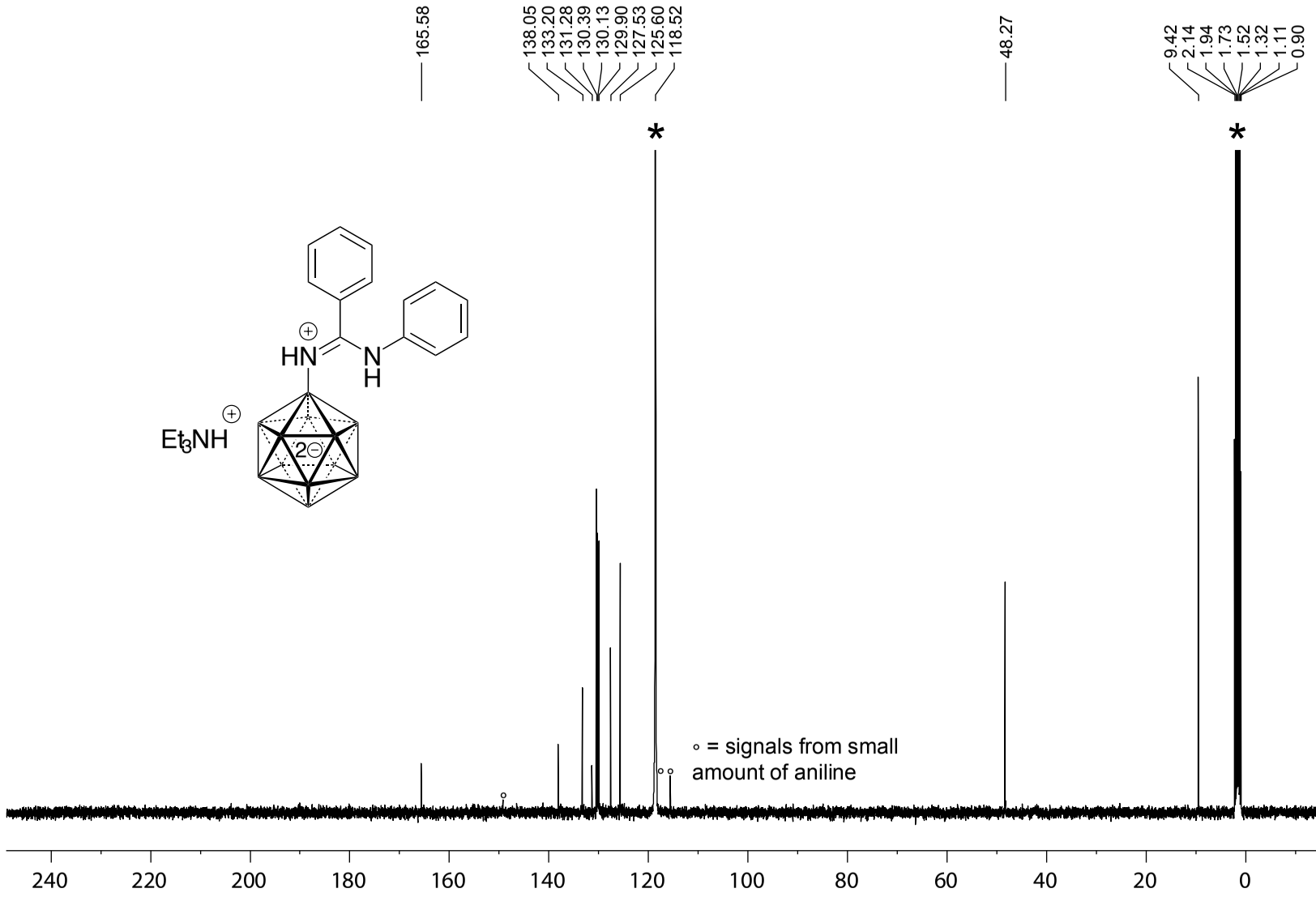

```
Current Data Parameters
NAME      20150313-syj-0078-1
EXPNO                       4
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150316
Time                  18.43
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                      32
DS                       0
SWH              32051.281 Hz
FIDRES            0.489064 Hz
AQ               1.0223616 sec
RG                     203
DW                  15.600 usec
DE                   6.50 usec
TE                  295.6 K
D1             5.00000000 sec
D11            0.03000000 sec

======== CHANNEL f1 ========
NUC1                   11B
P1                   10.00 usec
PLW1          75.00000000 W
SFO1         160.4615792 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PLW2          19.00000000 W
PLW12          0.42750001 W
PLW13          0.27360001 W
SFO2         500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF           160.4615993 MHz
WDW                     EM
SSB       0
LB                   20.00 Hz
GB        0
PC                    1.40
```

20160228-syj-0196-1, Et3NHB12NHC(C6H5)NHC6H5
20160228, 400 MHz, 1H{11B} NMR, 6.2 mg in 0.6 ml CD2Cl2*



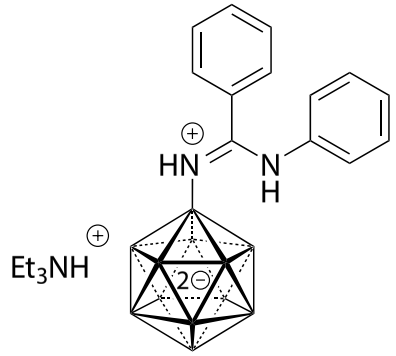

```
Current Data Parameters
NAME      20160228-syj-0196-1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20160229
Time                6.41
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 16384
SOLVENT           CD2Cl2
NS                    16
DS                     4
SWH             8012.820 Hz
FIDRES          0.489064 Hz
AQ             1.0223616 sec
RG                 107.6
DW                62.400 usec
DE                 6.50 usec
TE                295.3 K
D1           1.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 15.00 usec
PLW1         12.50000000 W
SFO1         400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp4
NUC2                 11B
PCPD2              90.00 usec
PLW2         52.96599960 W
PLW12         0.64477998 W
SFO2         128.3776050 MHz

F2 - Processing parameters
SI                 32768
SF          400.1300160 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20160228-syj-0196-1, Et3NHB12NHC(C6H5)NHC6H5
20160228, 100 MHz, 13C{1H} NMR, in 0.6 ml CD3CN*



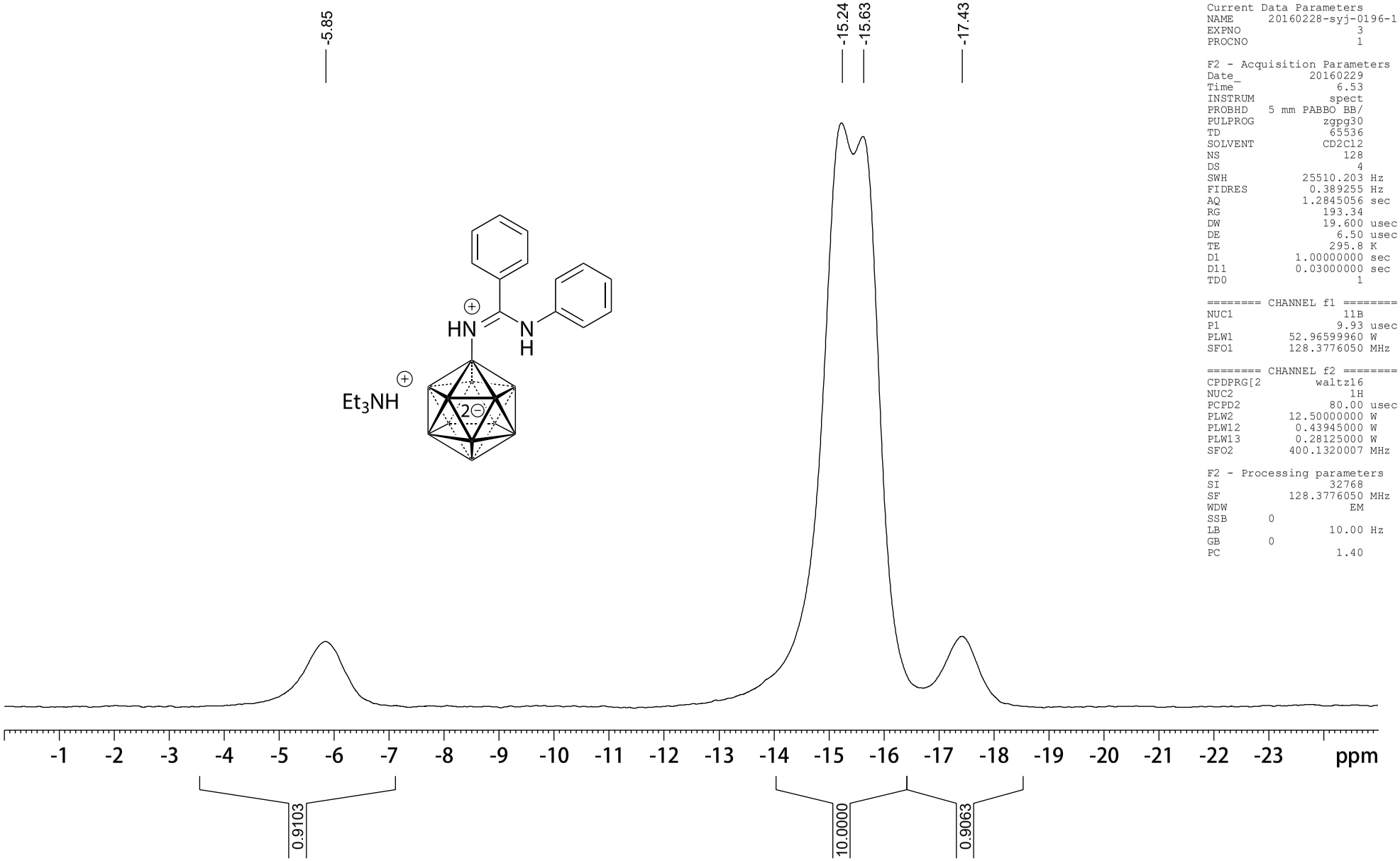

```
Current Data Parameters
NAME      20180531-syj-0196-C
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20180601
Time                 21.09
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                     512
DS                       4
SWH              29761.904 Hz
FIDRES            0.454131 Hz
AQ               1.1010048 sec
RG                  193.34
DW                  16.800 usec
DE                   6.50 usec
TE                  294.8 K
D1              1.50000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.00 usec
PLW1          53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                   1H
PCPD2                80.00 usec
PLW2          12.50000000 W
PLW12          0.43945000 W
PLW13          0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                   32768
SF           100.6126532 MHz
WDW                     EM
SSB       0
LB                    1.00 Hz
GB        0
PC                    1.40
```

20160228-syj-0196-1, Et3NHB12NHC(C6H5)NHC6H5
20160228, 128 MHz, 11B NMR, 6.2 mg in 0.6 ml CD2Cl2



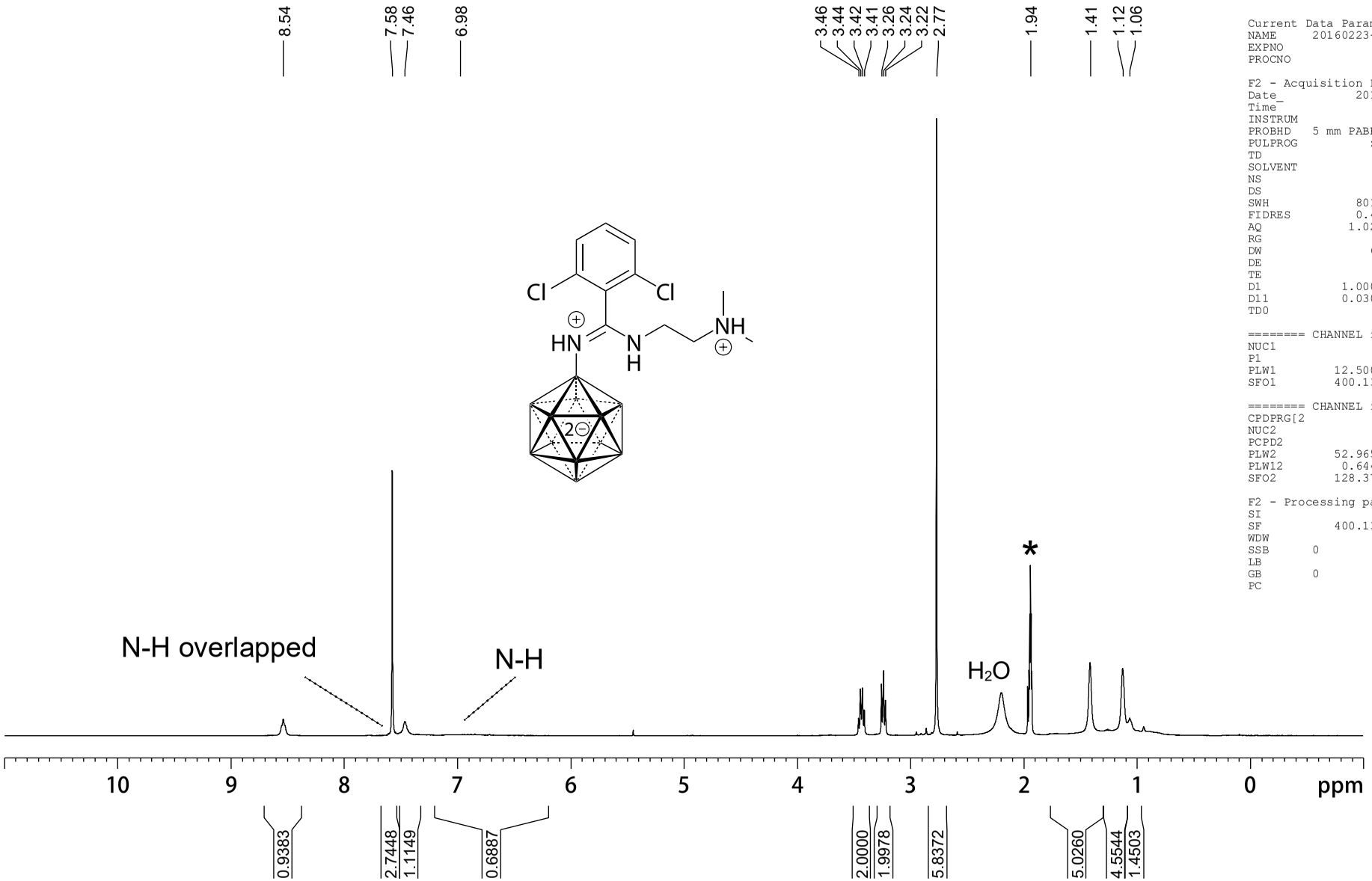

```
Current Data Parameters
NAME      20160228-syj-0196-1
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_              20160229
Time                   6.47
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                  zg
TD                    65536
SOLVENT              CD2Cl2
NS                      128
DS                        4
SWH               25510.203 Hz
FIDRES             0.389255 Hz
AQ                1.2845056 sec
RG                   193.34
DW                   19.600 usec
DE                    6.50 usec
TE                   295.0 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    11B
P1                     9.93 usec
PLW1          52.96599960 W
SFO1         128.3776052 MHz

F2 - Processing parameters
SI                    32768
SF           128.3776050 MHz
WDW                      EM
SSB       0
LB                   10.00 Hz
GB        0
PC                    1.40
```

20160228-syj-0196-1, Et3NHB12NHC(C6H5)NHC6H5
20160228, 128 MHz, 11B{1H} NMR, 6.2 mg in 0.6 ml CD2Cl2



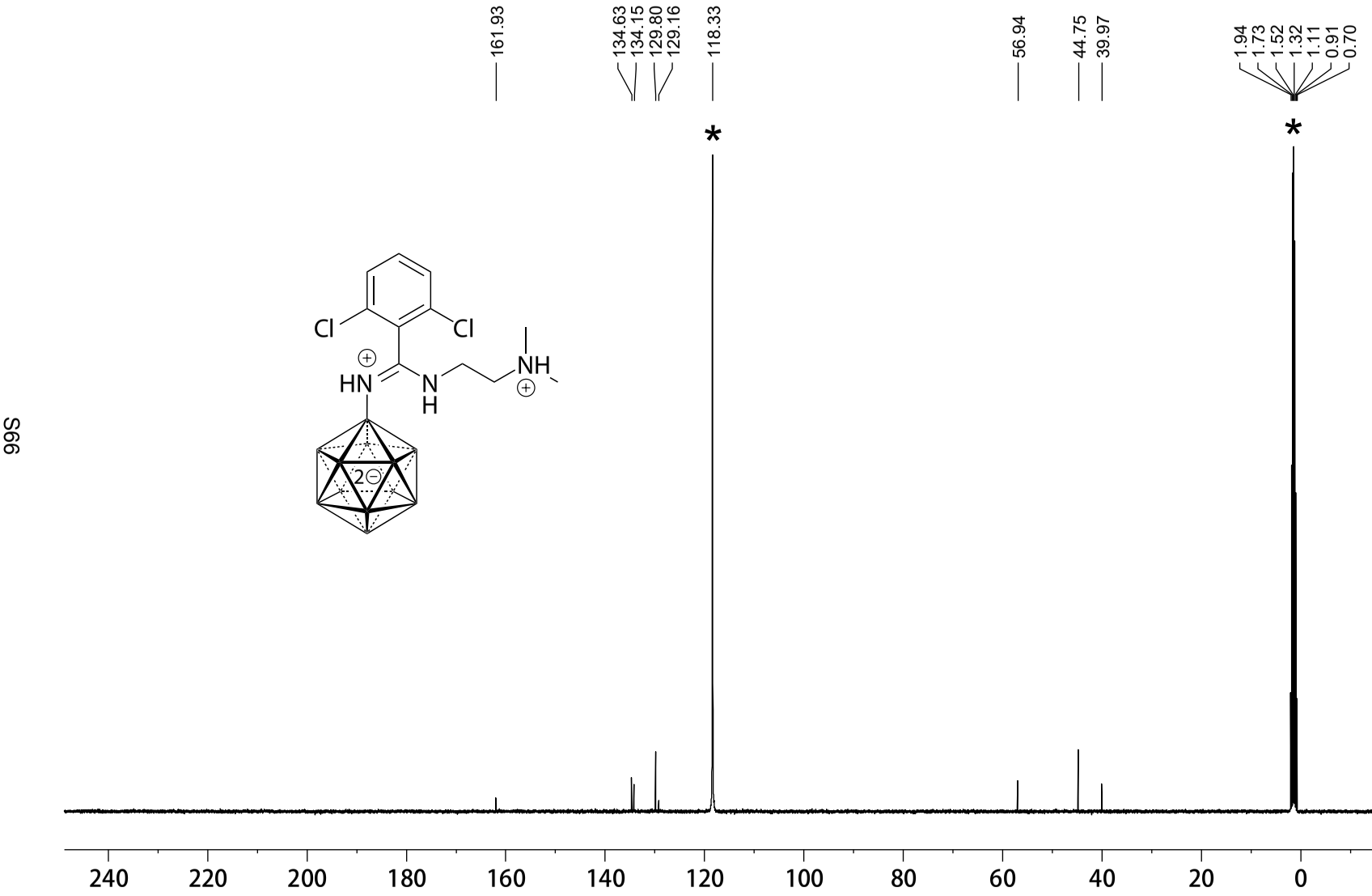

```
Current Data Parameters
NAME      20160228-syj-0196-1
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20160229
Time                   6.53
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT              CD2Cl2
NS                      128
DS                        4
SWH               25510.203 Hz
FIDRES             0.389255 Hz
AQ                1.2845056 sec
RG                   193.34
DW                   19.600 usec
DE                    6.50 usec
TE                   295.8 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    11B
P1                     9.93 usec
PLW1          52.96599960 W
SFO1         128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2           waltz16
NUC2                    1H
PCPD2                80.00 usec
PLW2          12.50000000 W
PLW12          0.43945000 W
PLW13          0.28125000 W
SFO2         400.1320007 MHz

F2 - Processing parameters
SI                    32768
SF           128.3776050 MHz
WDW                      EM
SSB       0
LB                   10.00 Hz
GB        0
PC                    1.40
```

20160223-syj-0193-1, B12NHC(C6H3Cl2)NH(CH2)2NH(CH3)2
20160223, 400 MHz, 1H{11B} NMR, in 0.6 ml CD3CN*



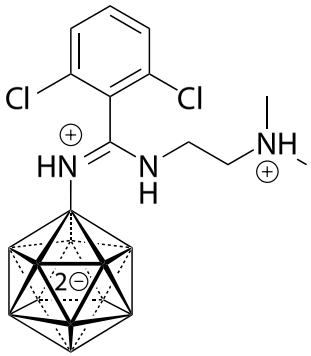

```
Current Data Parameters
NAME      20160223-syj-0193-1
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_            20160224
Time                1.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG           zgig30
TD                 16384
SOLVENT            CD3CN
NS                    16
DS                     4
SWH             8012.820 Hz
FIDRES          0.489064 Hz
AQ             1.0223616 sec
RG                 107.6
DW                62.400 usec
DE                 6.50 usec
TE                291.3 K
D1            1.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 15.00 usec
PLW1         12.50000000 W
SFO1         400.1320007 MHz

======== CHANNEL f2 ========
CPDPRG[2            garp4
NUC2                  11B
PCPD2              90.00 usec
PLW2         52.96599960 W
PLW12         0.64477998 W
SFO2         128.3776050 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300119 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

20160223-syj-0193-1, B12NHC(C6H3Cl2)NH(CH2)2NH(CH3)2
20160223, 100 MHz, 13C{1H} NMR, in 0.6 ml CD3CN*




```
Current Data Parameters
NAME      20180717-syj-0193-C
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_           20180718
Time                0.24
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CD3CN
NS                  512
DS                    4
SWH           29761.904 Hz
FIDRES         0.454131 Hz
AQ            1.1010048 sec
RG               170.36
DW               16.800 usec
DE                6.50 usec
TE               295.4 K
D1           1.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                10.00 usec
PLW1         53.00000000 W
SFO1         100.6228293 MHz

======== CHANNEL f2 ========
CPDPRG[2          waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2         12.50000000 W
PLW12         0.43945000 W
PLW13         0.28125000 W
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                32768
SF           100.6126732 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

20160223-syj-0193-1, B12NHC(C6H3Cl2)NH(CH2)2NH(CH3)2
20160223, 128 MHz, 11B NMR, in 0.6 ml CD3CN



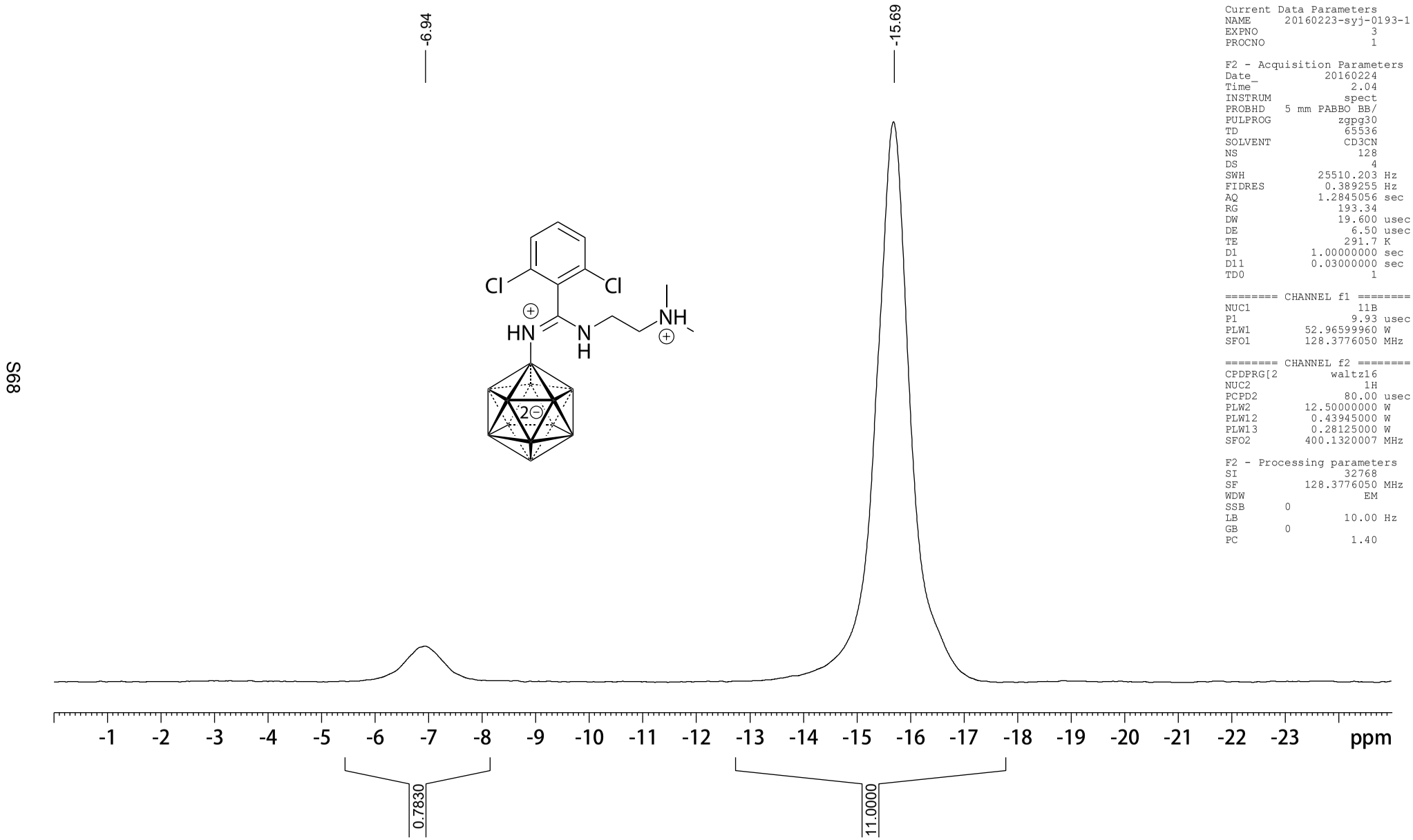
-6.93
-15.22
-16.14

```
Current Data Parameters
NAME      20160223-syj-0193-1
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_            20160224
Time                 1.58
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG                zg
TD                  65536
SOLVENT             CD3CN
NS                    128
DS                      4
SWH             25510.203 Hz
FIDRES              0.389255 Hz
AQ              1.2845056 sec
RG                 193.34
DW                 19.600 usec
DE                  6.50 usec
TE                 290.9 K
D1            1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   11B
P1                    9.93 usec
PLW1          52.96599960 W
SFO1         128.3776052 MHz

F2 - Processing parameters
SI                  32768
SF           128.3776050 MHz
WDW                    EM
SSB       0
LB                 10.00 Hz
GB        0
PC                  1.40
```

35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 ppm

0.8017
11.0000

20160223-syj-0193-1, B12NHC(C6H3Cl2)NH(CH2)2NH(CH3)2
20160223, 128 MHz, 11B{1H} NMR, in 0.6 ml CD3CN




```
Current Data Parameters
NAME      20160223-syj-0193-1
EXPNO                       3
PROCNO                      1

F2 - Acquisition Parameters
Date_              20160224
Time                   2.04
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                   65536
SOLVENT              CD3CN
NS                     128
DS                       4
SWH              25510.203 Hz
FIDRES            0.389255 Hz
AQ                1.2845056 sec
RG                   193.34
DW                   19.600 usec
DE                    6.50 usec
TE                   291.7 K
D1             1.00000000 sec
D11            0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      11B
P1                       9.93 usec
PLW1           52.96599960 W
SFO1          128.3776050 MHz

======== CHANNEL f2 ========
CPDPRG[2              waltz16
NUC2                       1H
PCPD2                   80.00 usec
PLW2           12.50000000 W
PLW12           0.43945000 W
PLW13           0.28125000 W
SFO2          400.1320007 MHz

F2 - Processing parameters
SI                      32768
SF            128.3776050 MHz
WDW                        EM
SSB       0
LB                     10.00 Hz
GB        0
PC                      1.40
```